Dmytro Snisarenko

Graduated in

Preparation and characterization of microfiltration flat polymeric membranes for biomedical applications

Dissertation for obtaining the Master degree in Membrane Engineering

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Abstract

The optimal methodology for flat supported hydrophobic microporous poly(vinylidene) fluoride (PVDF) industrial membranes (Fortex 0.1, Fortex 0.2, Fortex 1.2 and Fortex 3.0) production were developed with implementation of wet phase-inversion technique. The effect of different indicators of the production conditions, such as composition of polymer solution, quantity and type of additives, dissolving temperature, composition and temperature of the coagulation bath were studied. All the comparisons were performed in the narrow range of values in order to have better understanding of how slight deviation of each parameter can influence the performance of the industrially manufactured membrane.

During the development process it was observed that the increase of dissolving temperature results in formation of membrane with more open structure, justified by higher values of air flow (AF) and lower critical water entry pressure (water break through (WBT)). Moreover, the low molecular weight inorganic lithium salt has stronger effect on membrane performance than organic pore former applied.

After the optimization of production parameters for each type of membranes at the laboratory scale, the implementation of these conditions was realized at industrial scale. The good reproducibility of membrane characteristics prepared at laboratory and industrial scale was observed for three membrane types. The industrial trial for Fortex 0.2 membrane was not successful and this result was hypothetically related to the high viscosity of the casting solution. Additionally, it was demonstrated that absorbance of air moisture by polymer solution may significantly influence properties of manufactured membranes. Moreover, the industrially manufactured membranes as well as laboratory samples of Fortex 0.2 were characterized by means of scanning electron microscope, permporometry and Fourier Transform Infrared Spectroscopy. It was shown that usage of different solvent/non-solvent pairs (DMAc/water and DMAc/alcohol) was leading to the different membrane morphologies. Basing on permporometry test results, the largest active pores inside membranes were identified. Finally, it was shown that all the developed membranes possess β and γ crystalline phases and only Fortex 0.1 exhibited presence of α structure.

Key words: PVDF membrane, microfiltration, phase inversion, dissolving temperature, soft and harsh nonsolvents.

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Abbreviations

PS – Polysulfone

PES – polyethersulfone

PI – polyimide

PTFE – polytetrafluorethylene

PVDF – poly(vinylidene fluoride)

SEM – scanning electron microscopy

FT-IR – Fourier transform infrared spectroscopy

XRD – X-ray diffraction

DMAc – N,N-dimethylacetamide

HMPA – hexamethylphosphoramide

TMU – tetramethylurea

DMSO – dimethylsulfoxide

DMF – N,N-dimethylformamide

NMP – N-methyl-2-pyrrolidone

TEP – triethylphosphate

TMP – trimethylphosphate

PVP – poly(vinyl pirrolidone)

PEG – poly(ethylene glycol)

AF – air flow

WBT – water breakthrough

1. Introduction

1.1. Background and motivation

Over last decades, many researches have been performed in the field of novel membrane material development with the aim to achieve improved characteristics, such as high selectivity and high permeability. Nowadays, the membrane processes could be found in great variety of industrial process. Some of these applications require not just wonderful transport properties, but also high chemical, physical and thermal stability [1, 2]. Recently, poly(vinylidene fluoride) (PVDF) became one of the mostly used hydrophobic materials. Firstly, comparing with other materials such as polysulfone (PS), polyethersulfone (PES) and polyimide (PI), PVDF is relatively more hydrophobic [3]. Secondly, some other hydrophobic materials, such polypropylene, polyethylene, polytetrafluorethylene cannot be dissolved in commonly used solvents at low (room) temperatures. Thus, the membranes from these materials are produced by stretching and thermal methods, and the resulting membranes possess the symmetric structure with large pore sizes. In fact, PVDF is the only hydrophobic polymeric material, which could be dissolved in organic solvents with further asymmetric membrane preparation via phase-inversion process [4]. Moreover, this material attracted significant attention due to outstanding properties such as high mechanical strength, thermal and chemical resistance. Currently, PVDF membranes are extensively applied in various ultrafiltration and microfiltration processes, mainly for water and wastewater treatment. Additionally, this type of membrane material is a potential candidate to be used in membrane contactor applications [5, 6]. Finally, PVDF can be considered as pure polymer by possessing a low level of extractables, which allows its implementation in biomedical and bio-separation applications [3].

The membrane preparation basing on semi-crystalline polymer, such as PVDF is more difficult in comparison with glassy polymers. The main reason for such a complexity is in the fact that membrane could be formed by two different mechanisms: liquid-liquid demixing and/or crystallization (solid-liquid demixing) during phase-inversion processes [7]. By each mechanism specific membrane of different morphology could be obtained. The liquid-liquid demixing leads to the formation of asymmetric structure with dense layer on the top, while the crystallization process results in microporous structure with interconnected crystalline particles. Practically none of these mechanisms is an exclusive in the membrane formation, and its final structure is a result of combination of these mechanisms [4]. The domination of one mechanism over another is governed by different membrane preparation parameters, such as composition of dope solution, presence of additives, type of solvent and nonsolvent used, temperature of coagulation bath and dissolving temperature during the solution preparation. Thus, by varying each of these parameters can lead to the formation of membrane with completely different morphological and transport properties.

Nevertheless, all the published researches in this field up to now were discussing the influence of all these parameters at very large range of values. The influence of coagulation bath temperature on membrane properties was analyzed at the range 25°C – 85°C with step of 20°C [8]; effect of dissolving temperature in the range 20°C – 100°C again with step of 20°C [9]. While the industrial approach in membrane fabrication requires knowledge about these conditions influence in smaller range of values and about the possibility of process performance deviation with slight changes in manufacturing conditions. Thus, industry is more interested in research of the effect of these production parameters in the range of 5-10°C with the step of around 1-2°C. Similarly, the influence of coagulation bath composition on membrane properties is also analyzed mainly using ideal systems (i.e. pure water or pure alcohol [10]). In contrary, during the continuous process, such as industrial

membrane production, it is almost impossible to have 100% of non-solvent in the coagulation bath throughout the whole manufacturing process, because of continuous wash-out of solvent from the membrane. Thus, it is essential for the industrial process to find suitable coagulation bath initially composed of mixture solvent/nonsolvent, which composition could be controlled by simultaneous addition of non-solvent during the membrane production.

1.2. Objectives

The objectives of this work are to develop the methodology of PVDF membranes production with predefined characteristics at laboratory level and transfer the procedure to the industrial scale production.

In order to achieve final target the following tasks were performed:

1) The influence of the preparation conditions on the resulting membrane properties. The effect of mixing temperature during the dope solution preparation, presence and type of additives and composition of coagulation bath on the resulting membrane properties were evaluated;

2) Laboratory research results transfer to the industrial scale. The reproducibility of the membrane properties developed in the laboratory during industrial production was evaluated.

3) The morphological and structural characterization of newly developed membranes. All the membranes which possess the desired properties were characterized by means of SEM, permporometry and FT-IR.

2. Literature review

2.1. Microfiltration membranes

2.1.1. Historical development of membranes and membrane classification

The first information about membranes comes from 1748, when Abbe´ Nolet firstly used the term "osmosis" describing the transport of water through a semi-permeable diaphragm. Since that time the development of membranes had a lot of important milestones. One of them was the development of asymmetric membrane with thin dense top layer and porous support by Loeb and Sourirajan. This novel membrane gave ability to obtain one order of magnitude higher water flux at reverse osmosis process, meaning that this process became more practically and commercially attractive. Thus, a half of the century ago some fundamental research of the membrane science had already been conducted and some principals of membrane formation were investigated, but still membranes were used mainly in laboratory scale, due to problems with selectivity, cost and speed of the process. However, over the last half of the century the membrane science underwent great improvement in different aspects and the aforementioned problems were solved to the extent that membranes became extensively used in different separation processes [11].

In principle, all membranes can be classified according to the size of the pores on ones for: reverse osmosis, ultrafiltration and microfiltration. The range of pore sizes determining the application of membrane is depicted on Fig. 1, as well as the comparison with conventional filtration.

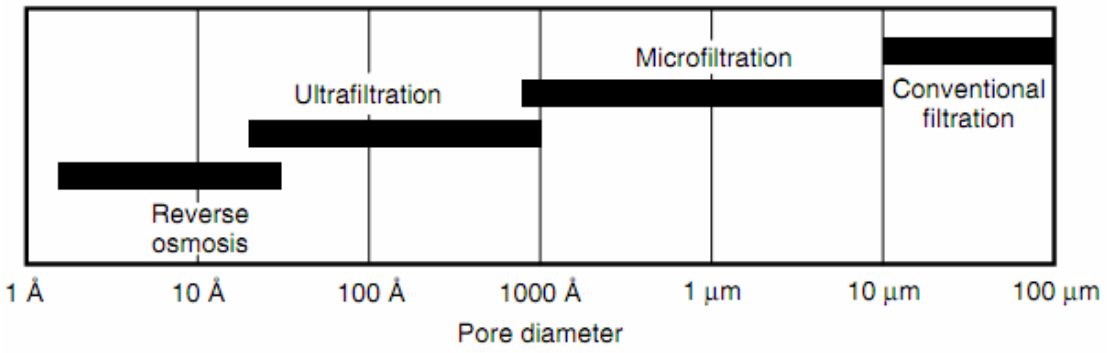


Fig. 1. Membrane classification basing on the pore size and their comparison with conventional filtration [11].

As it could be initially concluded from the Fig. 1 the reverse osmosis membranes possess pores of the size smaller than 2 nm (20 Å), however in real membranes no pores could be observed (membrane is dense) and the transport occurs through the free volume areas, while ultrafiltration and microfiltration membranes possess pores of the ranges 2 – 100 nm and 100 nm – 10 μm, respectively. In other words, in case when the particles with sizes over 100 nm should be removed from the solution, the more open – microfiltration membranes may be used. In case, when the macromolecules of molecular weight from 10^4 to more that 10^6 should be filtered out of the solution, the membrane should be denser, thus the ultrafiltration membranes are more suitable for this application [12].

2.1.2. Mass transport models through microporous membrane

Microfiltration is a pressure-driven process, which utilizes the microporous membranes which enable the passage of certain components and retains other compounds [13]. Two different microfiltration mechanisms could be distinguished: depth filtration and screen filtration [11]. The principles of both of them are schematically depicted on Fig.2. In case of the depth filtration, the removed particles stick inside the membrane due to larger sizes than membrane pores or adsorption to the wall of the pore. As a result the membrane pores become blocked and, therefore, membrane looses its initial transport

characteristics. This type of filtration model is more frequently observed. However, sometimes the microfiltration membrane has the smaller pores in the top layer than the size of the particles that have to be removed. In such a case the screen filtration is observed. This type of separation occurs on the surface of the membrane where filtered particles are accumulated [11].

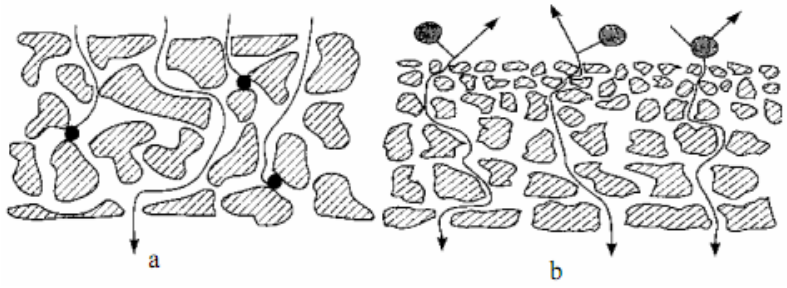


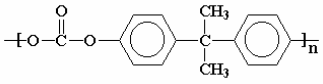
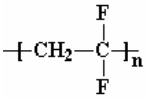
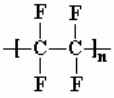
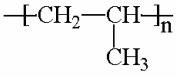
Fig. 2. Depth filtration mechanism (a) and screen filtration mechanism (b) [11].

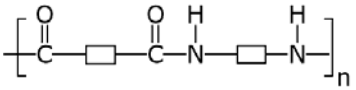
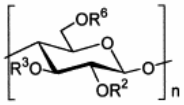
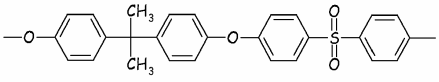
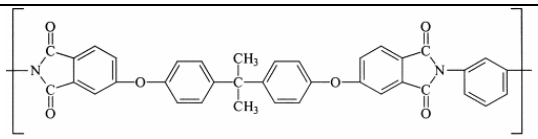
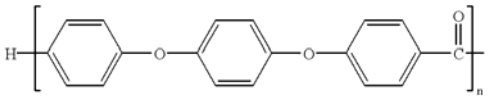
Aforementioned accumulation of particles on the membrane surface results in the phenomena called concentration polarization, the situation when flux through the membrane is decreased due to the formation of the "cake" (layer of particles stick to the membrane surface) that brings additional resistance to mass transfer. In other words, during the filtration process the solvent permeates through the membrane, while the solute is accumulated at the membrane surface leading to an increase in the solute concentration at the membrane surface and as a result the performance of membrane decreases significantly [12].

2.1.3. Materials used for microfiltration membranes preparation

The selectivity of microfiltration membranes are mainly determined by the pore size and by pore size distribution; however, choosing the appropriate material, such characteristics as adsorption, thermal and chemical stability should also be considered. These parameters are of high importance, because they determine the propensity of membrane towards the fouling (adsorption characteristics) and restrict the range of applications and possible cleaning methods applied for the membrane (chemical and thermal stability). In fact, the choice of material is first of all based on the fouling prevention and ease of cleaning process [12]. The typical materials used for the microfiltration membrane preparation are listed in the Table 1.

Table 1. Polymers for microfiltration membranes with respective chemical structure [4-12].

NAME OF POLYMER MATERIAL	CHEMICAL STRUCTURE
Polycarbonate	
Poly(vinylidene fluoride)	
Polytetrafluorethylene	
Polypropylene	

Polyamide	
Cellulose ester	
Polysulfone	
Poly(ether imide)	
Polyetheretherketone	

Each of material presented in the table above possesses one or more attractive properties. The first listed material – polycarbonate is usually selected due to its wonderful mechanical properties. Another important material for the microfiltration membrane preparation is cellulose and its derivatives (cellulose nitrate and cellulose acetate). These materials possess outstanding anti-fouling properties; however it is very sensitive to thermal and chemical influences [12]. Moreover, the polyamides should also be mentioned in the context of microfiltration membranes. According the chemical structure of monomers used for the polymer production the aromatic and aliphatic polyamides could be distinguished. For the purpose of microfiltration membrane production mainly the aliphatic polyamides are used. Although they possess good chemical stability, their thermal resistance is limited to the temperatures less than 100 °C which bring significant constrictions in terms of cleaning possibilities. Finally, the hydrophobic materials such as polytetrafluorethylene (PTFE), poly(vinylidene fluoride) (PVDF) and polypropylene are frequently used due to their relatively high crystallinity and high thermal and chemical resistance [12]. Since the poly(vinylidene fluoride) was used in current work, its chemical and thermal properties as well as its crystalline structure will be discussed in more details in the next chapters.

2.1.4. Porous supports used for membrane production

Porous support is a porous material used for composite membrane formation and improvement of their mechanical properties. Such a supports in the form of film of thickness 50-250 μm and different porosity are commonly produced from inert materials: polyethylene, polypropylene, aliphatic and aromatic polyamides etc. These materials are normally processed in films by means of physicochemical (i.e. hot pressing) or mechanical (sewing-knitting) methods. Moreover, sometimes other microfiltration and ultrafiltration membranes of different porosities are used as porous support.

In order to be used as support for asymmetric membrane the porous film should meet some requirements: 1) mechanically support thin selective layer of the membrane, 2) possess maximally open structure, which brings no additional resistance to mass transfer; 3) possess narrow pore size distribution, and, 4) be free from macrovoids, which can decrease the mechanical strength of membrane during use at high pressure applications [23].

In the process of composite membrane production, the polymer solution is cast on the surface of the support with subsequent use of phase inversion technique (dry, dry/wet or wet techniques). However

some other methods could be utilized: interfacial polymerization, graft polymerization of monomers from gaseous phase, plasma polymerization, and precipitation of different compounds on the surface or inside the pores of the support.

Finally, polypropylene or polytetrafluorethylene porous supports could be used for production of supported liquid membranes by impregnation of needed organic solvent or solution. In this case, the porous support acts as a matrix carrying the liquid, which perform the functions of membrane [24].

2.2. Properties of poly(vinylidene) fluoride

2.2.1. Thermal and chemical stability of poly(vinylidene) fluoride

Poly(vinylidene) fluoride (PVDF) is a semicrystalline polymer composed of repeating units -[CH_2-CF_2]- with the degree of crystallinity in the range of 35 – 70 %. Commercially available PVDF is manufactured by emulsion or suspension radical polymerization of 1,1-difluoroethylene [25].

It is well-known that polymers containing fluorine side groups are more thermally and chemically stable than non-fluorinated ones. This property is related to the fact that fluorine is more electronegative atom than hydrogen, and consequently, the C–F bond is more stable that C–H. By this the overall polymer chain gains superior stability characteristics in comparison to non-fluorinated hydrocarbons. Thus, PVDF withstand exposure to harsh thermal, chemical and ultraviolet environment. It could be used at temperature range from -62°C to 149°C. Moreover, the continuous use under temperature of 149°C results in no oxidation and no thermal degradation [26].

Some studies about thermal degradation of PVDF were performed to have better understanding of the limiting conditions for use of this material. The thermal induced polymer degradation was shown in several papers and all of them state that the mechanism for its degradation is the dehydrofluorination. This process could be intramolecular and intermolecular. Both variants are shown on the Fig. 3. The intramolecular dehydrofluorination leads to the formation of double (–C=C–) bond, while the intermolecular mechanism results in the polymer cross-linking [27].

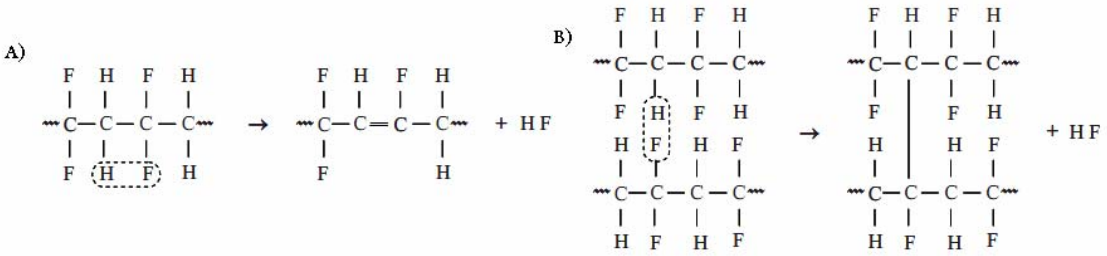


Fig. 3. The intramolecular (A) and intermolecular (B) mechanisms of dehydrofluorination.

Poly(vinylidene) fluoride is well-known for its high chemical resistance. However, some chemicals still can cause degradation of the polymer. According to the information presented on Arkema (one of main PVDF suppliers) web-site, different organic (strong acids, aldehydes, ketones and esters) and inorganic (salts and amalgams) compounds are not recommended to be used in contact with PVDF. Some of these chemicals can cause problems if they are used in pure state (acetophenone, chlorosulfonic acid), while some of them can have negative effect even in the form of aqueous solution (bytilamine, chloroacetic acid) [28].

Several research papers discussing the chemical stability of PVDF were published. In majority of these works sodium hydroxide was used to understand the mechanism and dynamics of polymer degradation. It was observed that under the alkali attack the PVDF changed the colour from white to brown and finally to black after several hours [29]. The changes of colour were related to the dehydrofluorination of PVDF with subsequent formation of double (–C=C–) and triple (–C≡C–)

bonds. This conclusion was justified by utilization of analytical tools, such as FT-IR and UV-visible spectroscopy [30]. Additionally, Benzinger *et al* [31] performed the study about the effect of different acids, bases and oxidants on PVDF membranes. It was demonstrated that PVDF was stable during long-term (several months) test to all the analyzed compounds apart from concentrated solutions of sodium hydroxide. Finally, Li *et al* [32] showed the influence of temperature on PVDF stability being in contact with sodium hydroxide solution. It was observed that elevated temperatures are favoring and facilitating the PVDF degradation due to attack of NaOH.

2.2.2. Crystallinity and polymorphism of poly(vinylidene) fluoride

The spatial distribution of fluorine and hydrogen atoms inside the polymer backbone determines the crystalline structure of PVDF. There are at least four different types of crystals which PVDF can form: α, β, γ and δ structures or phases [33].

The Fig.4 represents the atomic structure of α and β forms. The non-polar α form has monoclinic lattice with the trans-gauche (TGTG') conformation of polymer chain. The sigh G' shows the bond that turns the carbon polymer backbone for 60° angle from the plane. This deviation is governed by the repulsion forces present between the side groups of the polymer. In fact, such a conformation has lower energy, which could be an explanation for the fact that mainly α structure is forming from the polymer melt. This form is believed to be the most stable; however, other structures are also stable.

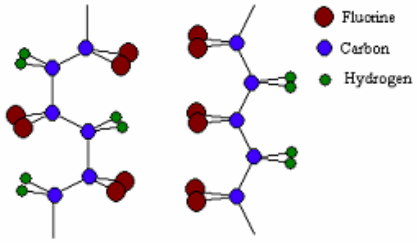


Fig. 4. The atomic structure of α (left) and β (right) forms of PVDF.

The polar β structure has planar zigzag form, where all trans bonds are remaining on the same plane. Two different organizations inside β structure are possible (Fig. 5): head-to-head and head-to-tail. The head-to-tail organization creates the very organized crystalline structure with improved packing density and reduced intermolecular strain. This type of organization possesses interesting piezo- and ferromagnetic properties. Basing on van der Waals forces, which are present between the atoms in PVDF chains, the β phase is more stable in intermolecular level, while α form is more likely to be formed at intramolecular level. The γ phase has orthorhombic lattice close to β one, but having slightly different sequence of trans and gauche bonds. This structural organization could be obtained by implementation of crystallization at high temperature. Finally, the δ phase is analogous to α phase with one main difference: δ phase is polar [34, 35]. In general, during the membrane formation α and β phases are mainly formed and understanding of how membrane preparation conditions can influence the formation of each phase is of high importance.

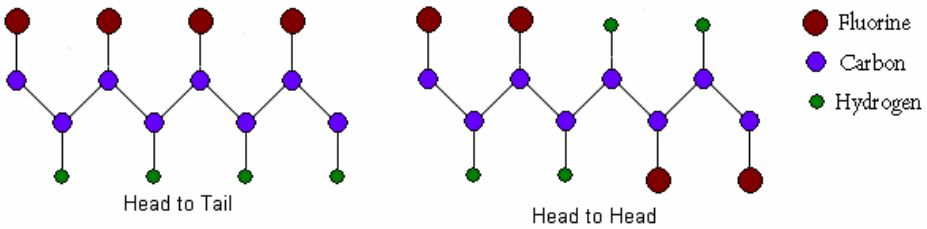


Fig. 5. Possible atomic organizations in β phase.

Since the PVDF backbone has only small side groups, this polymer is flexible, which gives ability to convert different phase from one to another. Some possible ways to alter the conformation of PVDF crystalline structure are shown on Fig. 6.

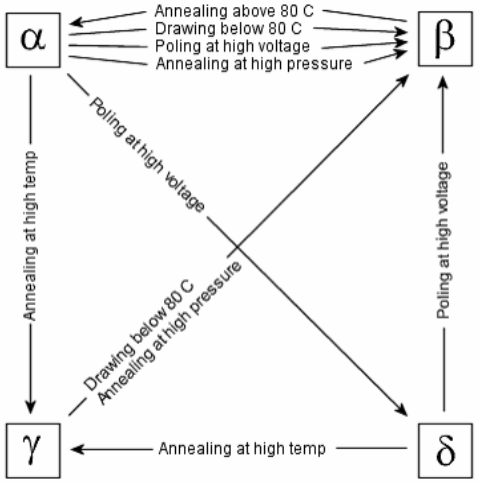


Fig. 6. Possible techniques used for phase transformation.

As it could be seen from this scheme that in order to convert one structure into another, different techniques could applied, such as drawing and annealing at different temperatures, applying electric field (poling) or annealing at high pressure [36].

Various analytical tools are used for the determination of different crystalline forms presence in the membrane. The main methods are Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). It was shown by Gregorio [37] that each phase has characteristic bands on IR spectra: *α* phase could be determined at 531, 612, 766, 795, 855, and 976 cm^{-1}, while the β phase – at 470, 511 and 840 cm^{-1}, finally, the presence of γ phase can be justified by the presence of bands at 430 cm^{-1}. The interpretation of XRD possesses rather large uncertainty, because lattice parameters of α and β structures are not uniform. Additionally, if both phases are present their diffractive peaks are overlapping in the area 2θ=20°. However, the presence of α phase can be justified by the presence of peak in the region 2θ=25-30° [38].

Numerous researches were performed to evaluate the influence of the membrane fabrication conditions on the formation of *α* and *β* phases, and ultimately on membrane characteristics. Tao *et al* [35] has demonstrated that the type and power of solvent has strong influence on the membrane crystalline phase. In their work, four organic solvents with different affinity to PVDF were used. It was demonstrated that the lower Hansen solubility parameter disparity of pair PVDF-solvent, the lower the β phase content in final membrane. Consequently, the better dissolved PVDF favors the formation of *α* phase during phase inversion process.

Wang *et al* [39] performed the research related to the coagulation bath temperature on the PVDF membrane crystallinity and presence of particular crystalline forms. According to this investigation, the highest degree of crystallinity is observed at lowest analyzed temperature. Concerning the *α* and *β* phases formation, it was demonstrated that at the highest temperature of coagulation bath favored the formation of solely *α* phase, while at the lowest temperature the mixture of both these phases was observed. Similarly, Cheng [8] performed the studies of coagulation bath temperature on the different crystalline phase formation. It was demonstrated that at higher temperature *α* is more likely to be formed, while in the membrane prepared at lower temperature spherical crystallites with *β* crystal structure are mainly observed.

Several researches were conducted in order to understand the effect of dissolving temperature on membrane properties. Lin *et al* [40] performed the study there the pair solvent/non-solvent of

dimethylformamide/1-octanol was used. The obtained results demonstrated that by increasing the dissolving temperature the larger spherical crystallites are obtained, while the total membrane crystallinity remains without significant changes. The same observations were reported by Wang *et al* [39] in their study of dissolving temperature on membrane morphology. It was shown that at higher temperatures larger PVDF particles were formed.

2.3. Phase inversion technique: immersion precipitation method

The history of PVDF membranes production started from around 1980s [3]. Currently, the most widespread technique in laboratory practice as well as in commercial membrane fabrication is phase inversion, in particular the immersion precipitation method, due to its simplicity and production process flexibility. These advantages give possibility to keep the cost of production on the low level, which is also attractive from commercial point of view [23].

Basically, the phase inversion process could be described by transformation of thermodynamically stable polymer solution from a liquid to a solid state under some influence. This transition may be induced by elevated temperatures (thermally induced phase separation), by influence of vapour (vapour-induced phase separation), by controlled evaporation of solvent or by immersion in the coagulation bath containing non-solvent (immersion precipitation). The later technique is the main one for the industrial production of the asymmetric membranes [3]. The schematic representation of phase inversion process is depicted on Fig. 7. The polymer solution, usually called as the casting or dope solution, is cast on the top of the appropriate support with use of a casting knife. The thickness of the polymer layer and, consequently, the thickness of the membrane are dependent on the adjustment of this casting knife. Then the film is immersed in a coagulation bath filled with nonsolvent where the polymer precipitation (phase inversion) occurs and the membrane is formed. The obtained membrane can further be subjected to washing, drying or/and post preparation treatment.

Various parameters can influence the morphology and the performance of produced membrane [12]. The influence of these parameters is not standard in all the cases and should be precisely studied for each system. Thus, the analysis of each parameter and its effect on the fabricated membrane is of high importance from both academic and industrial point of view.

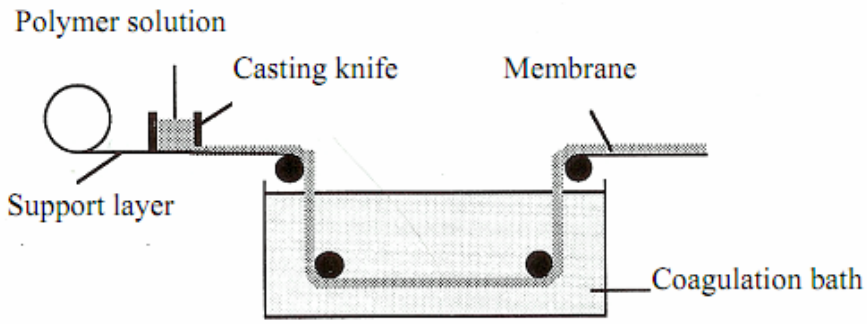


Fig. 7. Schematic representation of phase-inversion process [12].

As it was mentioned previously, PVDF is a semicrystalline polymer, and its phase separation process is more complex in comparison to amorphous polymers. Numerous research groups performed the studies of the influence of different membrane production conditions on its final morphology and performance. The main parameters capable of affecting the PVDF membrane structure are: choice of solvent, composition of dope solution, presence of additives in the casting solution, dissolving temperature, choice of non-solvent, temperature of coagulation bath. The influence of each of them will be discussed herein in more details.

2.3.1. Mechanisms of membrane formation during phase inversion: thermodynamic and kinetic aspects

The characteristics of membrane prepared with use of phase inversion technique are dependent on: 1) thermodynamic aspects of membrane formation, and 2) kinetics of the system, the rate of phase inversion during immersion precipitation [41]. In order to have understanding of the thermodynamic aspect of membrane formation, the ternary phase diagram can be used as a useful source of information [12]. The kinetic aspect should be understood as the rate of solvent-nonsolvent exchange, which is an important factor influencing the structure of pores in the fabricated membrane [42].

2.3.1.1. Thermodynamic aspect of membrane formation

From the thermodynamic point of view, the system polymer-solvent-nonsolvent could be depicted in a ternary phase diagram (Fig. 8). This diagram gives information about system composition, its behavior in response on addition of any of its components and enables prediction of phase state of the system depending on its composition.

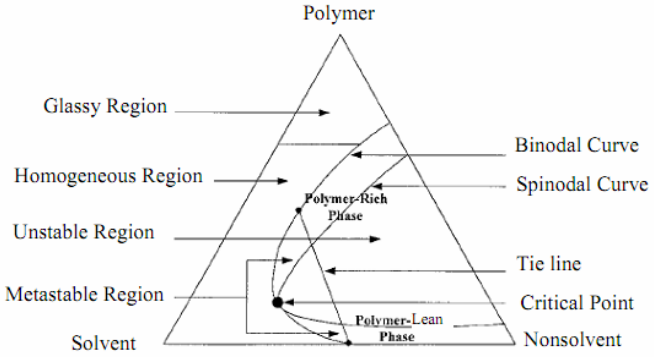


Fig. 8. Ternary diagram of polymer-solvent-nonsolvent system [43].

The corners of the triangle represent pure components (polymer, solvent and nonsolvent), the axes of the triangle depicts the binary combinations of connected compounds, and any point inside the triangle shows the composition of the system containing all three components [44]. The key elements of this diagram are: binodal curve, spinodal curve, a critical point, tie lines, and a glassy (gelation) region. [43]. The binodal curve separates the homogeneous and metastable regions. The former region represents the range of system compositions, where it is thermodynamically stable, all three components are miscible and no apparent changes occurs with the course of time, while in latter region the system undergoes the phase separation by nucleation and growth. This behaviour is observed until system reaches spinodal curve, which represents the boundary of unstable region, where the system is separated on two equilibrium phases (polymer-rich and polymer-lean) due to thermodynamic instability. The points on the binodal curve showing the compositions of these phases are connected by tie lines. Finally, the point where binodal and spinodal meet is called the critical point [43, 45].

The system transition from stable state to the unstable is usually induced by changes in temperature or in the composition [46]. Two different phase transition mechanisms can be distinguished: liquid-liquid demixing and solid-liquid demixing (crystallization). The former mechanism could be observed in case of both amorphous and crystalline polymers, while the latter should be considered only for crystallizable ones [47]. The liquid-liquid demixing results in the cellular morphology with pores from polymer-lean phase and the membrane matrix from the polymer-rich phase; while the membrane obtained as a result of solid-liquid demixing usually consists from linked particles (crystallites). Since the process of crystallization requires the specific orientation of polymer chains for the initial nucleus formation and its subsequent growth, the solid-liquid demixing takes longer period of time [48]. Nucleation and growth should be the expected mechanism when a system leaves the

thermodynamically stable conditions slowly and enters the metastable region of the phase diagram between the binodal and the spinodal curves. In such a situation new nuclei are formed and become stable if the activation energy for nuclei formation is higher than their surface free energy [47].

Two different types of nucleation and growth can be distinguished in case of solid-liquid demixing phase separation process. If the system enters the metastable region of the phase diagram below the critical point, nucleation and growth of the polymer-rich phase occur in polymer-lean phase. In this case, the powdery agglomerates with low integrity will be obtained and, thus, membrane is not formed. In contrary, if the system enters the metastable region above the critical point the opposite phenomena is observed – polymer-lean phase is nucleating and growing in polymer-rich phase. As a result the matrix of membrane is formed from the polymer-rich phase, while the porous structure is created from the polymer-lean phase [43].

Moreover, going back to liquid-liquid demixing mechanism, in order to predict the morphology of the fabricated membrane, it is important to know the behaviour of polymer solution upon its contact with nonsolvent. In particular, the changes in its composition with time are of high importance. Depending on the time needed by system to move from stable to unstable region one can distinguish two different ways: instantaneous demixing and delayed demixing. The former one means that the membrane structure is formed immediately after its contact with the nonsolvent, while the latter way takes some time before the membrane get the final structure [12]. The composition path of the system in cases of instantaneous demixing and delayed demixing are depicted on Fig. 9.

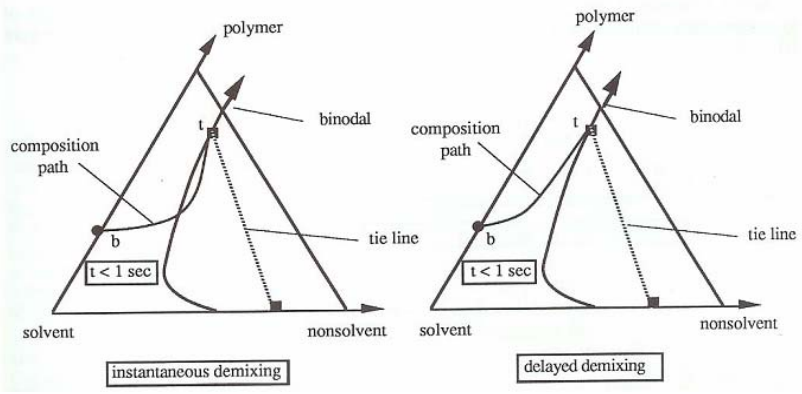


Fig. 9. Composition path of the casting solution in instantaneous (left) and delayed demixing (right) [12].

Since the process of the exchange between cast film and coagulation bath starts at the interface polymer solution/nonsolvent, the first changes in composition are observed in the top of the membrane. On the Fig. 9 the point "t" represents the composition of the membrane on the upper layer, while point "b" respects to the bottom of the membrane. Additionally, according to the Fig. 9, in case of the instantaneous demixing, layer of the film located just beneath the top layer have crossed the binodal curve meaning that the liquid-liquid demixing started less than 1 second after the immersion in the bath with nonsolvent. In contrast, in the case of delayed demixing, all layers beneath the top layer are still in the one-phase region. Thus, it could be stated that no demixing occurs immediately after immersion. With the course of time, the compositions beneath the top layer will cross the binodal curve and, consequently, process of the liquid-liquid demixing will occur [12].

2.3.1.2. Kinetic aspect of membrane formation

Apart from the thermodynamic effects, the kinetic aspects should be also taken into account in order to predict and to explain the structure of the fabricated membrane. The skin layer and the structure of supportive layer are governed by: solvent-nonsolvent exchange rate during the polymer precipitation process and, if additives are presence, the leaching rate of additive from polymer film [49].

Up to now, two different approaches to investigate the dynamics of phase separation are developed. The first approach, usually referred as cast-leaching, means the monitoring of the coagulation bath composition. Several works showed that the outflow of a solvent from a cast film has the diffusion character [50]. In other words, the mass transfer of solvent in coagulation bath from the polymer solution is rate limiting step in coagulation process. In the second approach, the optical microscopy is applied to follow the process of polymer film coagulation [51]. The studies in the frame of this approach demonstrated that the propagation rate of the film precipitation front was proportional to the square root of time ($t^{1/2}$) up to 60% of the thickness and that the mass transfer had the diffusion character. Additionally, several different models describing the solvent-nonsolvent exchange were developed [49]. Finally, in 1996 the model describing the polymer concentration at the interface coagulation bath/cast film was proposed [52]. The application of this model brought to the conclusion that different solvent-nonsolvent systems results in different membrane structures.

2.4. Influence of preparation conditions on membrane morphology and performance

As it was discussed previously, various parameters of phase-inversion process can influence the structure and performance of fabricated membrane. Numerous research groups presented results of their studies of preparation conditions effect on the membrane morphology and separation characteristics. All these research results could be grouped with respect to the specific analyzed parameter.

2.4.1. Effect of solvent

The choice of solvent is a crucial parameter that determining the membrane appearance and performance. The suitable solvent enables uniform distribution of polymer molecules in the solution, while the bad solvent use will lead to the aggregation of polymers chains. It was identified that eight solvents out sixty four analyzed can be considered as good solvents for PVDF [53]. They are N,N-dimethylacetamide (DMAc), hexamethylphosphoramide (HMPA), tetramethylurea (TMU), dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), triethylphosphate (TEP) and trimethylphosphate (TMP). The propensity of each of these solvents to dissolve PVDF can be characterized by means of Hansen solubility parameters (Table 2 [54]). The higher value of δ_t means the higher solubility power of particular solvent.

Table 2. Hansen solubility parameters of common solvents for PVDF

Solvent	***Total solubility parameter, δ ($MPa^{1/2}$)***
N,N-Dimethylacetamide (DMAc)	22.7
N,N-Dimethylformamide (DMF)	24.8
Dimethylsuloxide (DMSO)	26.7
Hexamethyl phosphoramide (HMPA)	23.2
N-methyl-2-pyrrolidone (NMP)	22.9
Tetramethylurea (TMU)	21.7
Triethyl phosphate (TEP)	22.3
Trimethyl phosphate (TMP)	22.3

The effect of solvent on the membrane morphology was performed by Yeow *et al* [55]. Authors used four different good solvents (DMAc, DMF, NMP and TEP). It was demonstrated that membrane obtained from the TEP solution possessed the symmetric sponge-like structure, while three other membranes were of asymmetric structure with dense skin layer and macrovoids beneath. These observations were related to the differences in solvent powers and mutual affinity between solvent and nonsolvent. Thus, TEP being the weakest solvent and having the weakest affinity to used nonsolvent (water) gave ability to obtain structure, which was completely different from the other.

The effect of four different solvents on the PVDF crystalline structure was analyzed by Tao and coworkers [35]. The used solvents were: triethylphosphate (TEP), hexamethylphosphoramide (HMPA), trimethylphosphate (TMP) and N,N-dimethylformamide (DMF). The results of this work demonstrated that the polymorphism of PVDF membrane is dependent on the solubility power of the solvent. The better solvents, which were leading to more complete dissolution of polymer, were favoring the α phase formation, while the poorly dissolved PVDF solution tended to form the β phase.

2.4.2. Effect of additives in the casting solution

The addition of additives to the dope solution is one way to improve or change the performance of ultimate membrane. The additive can perform such functions as: pore formation, increase of solution viscosity and/or facilitate the process of phase inversion [3]. Additives used in PVDF membrane preparation could be divided into four categories: 1) polymeric additives, such as poly(vinyl pirrolidone) (PVP) and poly(ethylene glycol) (PEG); 2) weak nonsolvents such as glycerol; 3) weak cosolvents such as ethanol and acetone; and 4) low molecular weight additives, such as LiCl and $LiClO_4$ [55].

The addition of PVP or PEG leads to the increase of solution viscosity. As a result the miscibility between the cast solution and nonsolvent is reduced. Thus, the kinetics of phase separation became hampered, while the thermodynamic aspect of membrane formation receives the dominating role [55]. In terms of membrane structure, it was demonstrated that addition of PVP leads to the decrease of mean pore size and the increase of the effective porosity [56]. Since PVP is of hydrophilic nature its presence in the casting solution enhance the influx of nonsolvent during the coagulation process, which leads to the formation of finger-like macrovoids [3, 55]. Additionally, PVP is a high molecular weight compound, meaning that it can't be completely washed out from the membrane. The leftovers of this additive in the ultimate membrane can change its hydrophobicity and, consequently, make it inappropriate for the membrane distillation process [4].

The effect of glycerol addition to the casting solution was studied by Shih and coworkers [57]. In their work they used two different solvents for PVDF dissolution and water as nonsolvent. The results of this research demonstrated that membranes obtained using TEP as a solvent possessed increased mean pore size and effective porosity with increase of glycerol content in the casting solution. In contrary, while using DMSO as a solvent by increasing the glycerol content in dope solution the ultimate membranes with increased mean pore size and decreased effective porosity were obtained. These observations were related to different mutual affinity between used solvents and nonsolvent.

The effect of LiCl on casting solution, membrane morphology and performance was shown in numerous research papers. Its addition to the dope solution leads to the significant increase of viscosity. This effect is usually related to the formation of complexes between Li^+ and polar solvent (i.e. DMAc) or/and the electron-donor group of PVDF [58]. The increase of LiCl content in casting solution leads to the formation of macrovoids, and, consequently, to higher porosity and increased maximum pore size [59]. This effect is related to the fact that LiCl has a good affinity to water, meaning that during the coagulation process the inflow of water is enhanced and, therefore, the interconnected structure is obtained [60]. However, this behavior is observed only up to certain content of LiCl in dope solution. It was shown that at higher concentration the formation of macrovoids is suppressed [61]. This phenomenon is attributed to the competition between thermodynamic and kinetic effects during the phase inversion process. Thus, it was concluded that at lower LiCl concentration the dominant mechanism was instantaneous liquid-liquid demixing, while at higher additive content the membrane formation was mainly governed by delayed demixing process.

Another salt of litium ($LiClO_4$) is also widely used in PVDF membrane formation. The addition of $LiClO_4$ had the same effect on solution viscosity as of LiCl, due to same aforementioned reasons. At low content of $LiClO_4$ in dope solution the increase of mean pore size of and more sharp pore size distribution were observed, while the higher content this salt can have the opposite effect. Finally, the

increase of $LiClO_4$ content in the casting solution leads to the larger macrovoids formation in the ultimate membrane [62].

2.4.3. Effect of dissolving temperature

The effect of PVDF dissolving temperature during the casting solution preparation on the membrane morphology was studied in some works. Wang *et al* 2009 [63] performed the research, which demonstrated the changes on the morphology of PVDF membranes prepared from four different temperatures (50°C, 70°C, 90°C and 120°C) with water as a nonsolvent. It was shown that all the membranes were of an interconnected structure. The cavities between the particles were of different size: starting from around 0.3-0.6 μm at the lowest dissolution temperature and increasing three to four times with every step of temperature increase. Additionally, Mi-mi Tao *et al* [35] applied three different dissolution temperatures (50°C, 80°C and 110°C) for the casting solution preparation with further analysis of their influence on membrane morphology and crystalline structure. It was concluded that the total number and the volume of macrovoids inside the membrane is increasing with the increase of dissolution temperature. Moreover, it was found that lower temperature favors the formation of β phase, while the higher temperature leads to the better dissolution of PVDF and, therefore, enhanced mobility of polymer chains which results in their arrangement in α form. Finally, Ahmad *et al* [9] studied the effect of PVDF dissolution temperature on the pore size distribution. The author applied various temperatures in the range from 20°C to 100°C with the step of 20°C. It was found that the narrow pore size distribution is obtained only at temperatures not exceeding 40°C, while at temperatures greater than 60°C the pore size distribution became much wider with the shift of average size towards larger pores.

2.4.4. Effect of coagulation bath composition

As it was stated previously, since PVDF is a semi-crystalline polymer, the membrane formation process occurs via two different mechanisms. In the immersion-precipitation method of phase inversion the composition of coagulation bath has a crucial effect on the ultimate membrane morphology and performance. In general, all the nonsolvent applied for the PVDF precipitation could be divided into two groups: strong and weak (soft) ones [23]. The typical example of strong nonsolvent is water and its presence in coagulation bath favor the membrane formation via instantaneous liquid-liquid demixing which results in asymmetric membrane structure with dense layer on the top and finger-like structure beneath [10]. On the other hand, the addition of solvent in coagulation bath can lead to the delayed demixing. Choi *et al* [6] demonstrated that by increasing the DMAc content in the coagulation bath the membrane morphology was gradually changing from finger-like to the sponge-like structure. This observation was attributed to the changes from the instantaneous to the delayed demixing process. In other words, the precipitation power of coagulation bath was approaching the one of weak nonsolvent.

In general, the typical compounds, referred as weak nonsolvent, are alcohols of different structure (C1-C8) [28]. It was demonstrated that using 1-octanol the membrane with symmetric structure composed of identical spherical particles was obtained indicating that the crystallization preceded liquid-liquid demixing [58]. Additionally, Deshmukh and Li [56] performed the study where for the PVDF membrane formation the mixture of strong and soft nonsolvents at different ratios was used. In particular, the effect of ethanol concentration in the mixed ethanol/water coagulation bath on membrane performance and morphology was evaluated. It was shown that by increasing the ethanol concentration from 0% to 50% the finger-like structure was changed to the sponge-like structure.

Finally, in order to have better understanding of difference between strong and soft coagulants from the quantitative point view, their solubility parameters should be compared with the one of PVDF. Thus, the solubility parameter difference between PVDF and isopropanol is 1.3 $(J/cm^3)^{1/2}$, while this difference between PVDF and water is equal to 24,5 $(J/cm^3)^{1/2}$ [64]. The lower the difference between

solubility parameter is, the slower is the process of liquid-liquid demixing, and, thus, the crystallization has enough time to occur and as a result the symmetric structure is formed.

2.4.5. Effect of coagulation bath temperature

The temperature of coagulation bath is one of the key parameters defining the ultimate membrane properties. Cheng [30] analyzed the coagulation bath temperatures in the range from 25°C to 85°C. It was demonstrated that the lower temperature was leading to the formation of sponge-like structure, while at elevated temperatures the finger-like structure was created. This result was explained by means of kinetics. At higher temperatures the exchange of solvent and nonsolvent is facilitated, and, therefore, the liquid-liquid demixing occurred at the early stage of membrane formation process. In contrary, at lower temperatures the mutual diffusion of solvent and nonsolvent is hindered, thus the dominating mechanism of membrane formation is crystallization. The same observation was done by Wang *et al* [65]. The authors analyzed three different temperatures of coagulation bath (15°C, 25°C and 60°C). The results of their research also revealed that due to differences in kinetics of solvent and nonsolvent exchange the different membrane morphology was obtained. Finally, the temperature of coagulation bath is also influencing the crystallinity of PVDF membrane. This effect in more details was described previously in chapter 2.2.2.

2.5. Microfiltration membrane characterization

The microfiltration membranes can be characterized with use of different techniques and their choice is normally made basing on the required membrane characteristics. Required characterization parameters for membranes could be divided into two groups: 1) structure-related parameters: morphology, pore size and pore size distribution, effective surface porosity, total porosity, crystalline structure (in case of semi-crystalline polymers) etc; and 2) permeation-related parameters: membrane permeability, molecular weight cut-off etc.

2.5.1. Mean pore size and effective surface porosity

Mean pore size and effective surface porosity are two important parameters influencing the permeation rates through the membrane. The gas permeation method is one of techniques applied to evaluate these two membrane parameters. There are two possible mechanisms of gas transport through the membrane: Knudsen diffusion and Poiseuille (viscous) flow [66]. The ratio of the pore radius (r) to the mean free path of gas molecule (λ) is the parameter which determines the mechanism of gas permeation [67]. In case $r/\lambda>1$, the dominating mechanism is the Poiseuille flow, while in case $r/\lambda<1$, the mechanism determining the gas permeation is Knudsen diffusion. The total gas flux in case of both mechanisms can be described as:

$$Q_{vis} = \frac{r^2(P_1^2 - P_2^2)}{16l\mu RT} \quad (1)$$

$$Q_{KD} = \frac{8r(P_1 - P_2)}{3l(2\pi MRT)^{1/2}} \quad (2)$$

where l is the length of the pore, μ is the gas viscosity, M – molecular weight of the gas, R is the universal gas constant, P_1 and P_2 are the gas pressure on the feed side and the permeate side, respectively.

2.5.2. Pore size distribution

Another important parameter in microporous membrane characterization is pore size distribution. Practically, the sizes of pores inside the membrane are not completely uniform and are present in a specific range of sizes (Fig.10).

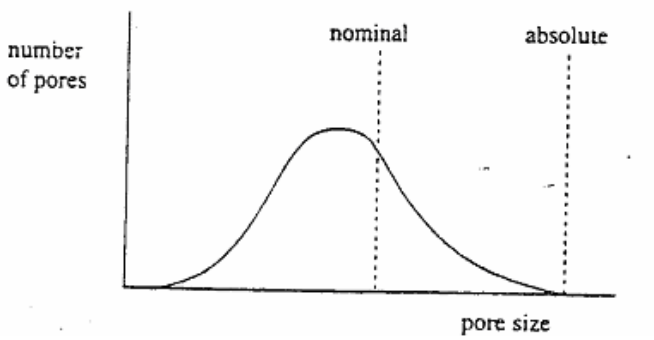


Fig. 10. Schematic representation of pore size distribution [12]

As it could be seen from the figure above, two different specific pore sizes could be determined: nominal and absolute. The data about absolute pore size gives ability to tell that particles of the same or larger size are completely retained by membrane, while the nominal size indicates that particles of this size or larger are retained up to 95% to 98% [12].

There are number of methods allowing the determination of pore size distribution. The main of them are: gas-liquid displacement, mercury porosimetry, thermo-porometry, permporometry etc [68]. Each of these methods are based on the measurements of pressure needed to force a non-wetting liquid to flow through the pores of a membrane. The obtained data about applied pressure and corresponding membrane filling with the non-wetting liquid can be converted to the knowledge of pore sizes by applying the next equation:

$$\Delta P = \frac{2\gamma \cos\theta}{r} \tag{3}$$

where γ is the surface tension of the liquid, θ is the contact angle of the liquid on the inner surface of the pore, r is the radius of the cylindrical pore.

In more details the aforementioned techniques normally used for the determination of pore size distribution are described elsewhere [68].

In case of hydrophobic membranes the same principle is applied in the critical water entry pressure measurements. The water is brought to the direct contact with membrane surface and pressure is applied. The pressure at which the first bubble of water permeates though the membrane is called critical water entry pressure (CEP_w). Knowledge about CEP_w enables the determination of the largest pore present in analyzed sample by implementing equation similar to previous one:

$$\Delta P = -\frac{2\gamma \cos\theta}{r_{\max}} \tag{4}$$

where r_{max} represents the maximal pore size of the sample.

2.6. Hydrophobic microfiltration membranes for medical applications

Hydrophobic polymeric membranes are extensively applied in medical devices to provide sterile barriers between the atmosphere and device interiors. These membranes, sometimes referred as vent membranes, are blocking liquids, while allowing the passage of the air. They are mainly used as air filters, which are able to eliminate potentially infectious aerosols and particles. In fact, a single venting membrane can substitute the system of valves and filters. The applications of such filters include in-line sterile barriers (transducer protectors, vacuum-line protectors), liquid shutoff valves (suction canister vents), air inlet valves (intravenous spike vents), air vent valves (intravenous filter vents), container filling vents (urine bag vents), sterile wound dressings, gas sterilization devices for blood oxygenation etc [69].

Sometimes such filters are initially connected to intravenous tubing, while others must be attached just before use. In general, the size of filter membranes is varying from 5 to 0.22 μm. Theoretically, filters with pore size range of 1 to 5 μm are able to retain large particles and debris, but not fungi or bacteria. Filters that possess pores around 0.45 μm enable the removal of fungi and most bacteria. Finally, the filters, pore of which are not exceeding 0.22 μm, remove all fungi and bacteria [70]. In addition, the latter type of microporous membranes is considered sterilizing grade. Moreover, some suppliers also produce 0.1 μm membranes to insure the complete mycoplasma removal. Since under the certain pressure membrane wetting may occur, and consequently, bacteria will be able to pass through, majority of medical device manufacturers utilize the vent membranes with pore sizes in the range 0.1 or 0.2 μm [71].

However, it should be noted that the mechanism of bacterial retention by hydrophobic membranes from a gas stream is different in comparison to hydrophilic membranes in liquid filtering. Microorganisms usually are not present in free state in the air; they are usually attached to particles of aerosol or of the dust. Thus, during the air filtering majority of pathogens can be retained by membrane with pore sizes larger than microorganisms. In some cases, even membranes with pore sizes of 5 μm perform the 99.99% bacterial retention. Consequently, membranes with larger pore sizes may be used in specific cases having an advantage of higher air flow per unit of time [71].

In such application as intravenous injections, an injection solution has to be delivered with even pace. However, when the solution is delivered from a rigid vessel, air should flow into this vessel in order to prevent the vacuum formation inside the system. In this type of containers, the special sterile inlet for the air should be present and vent membranes offer such a possibility. In case of their usage, the air is sucked inside the vessel only when the liquid is delivered to the patient; when system is closed and the level of liquid is stable, no air is permeating through the vent membrane. Additionally, the hydrophilic filters used in intravenous systems apart from bacteria and particles remove air from the injection solution, and these formed air bubbles has to be removed from the system. In such cases, the use of vent membranes is also a good solution to the emerging problems [69].

Finally, apart from considerations of bacterial retention mechanism, the venting membranes selection should be also based on its intended use. Different solutions in terms of composition and nature can be in contact with the membrane (water, buffer solution, solution containing the proteins or drugs, blood, urine etc). Every solution has specific propensity towards wetting the membrane and, therefore, causing its failure. Thus, in some cases, a vent membrane is placed above the liquid surface in order to be dry throughout the usage period, while in other cases, the solution may contact the membrane [71].

3. Materials and methods

3.1. Materials

Poly(vinylidene fluoride) (PVDF) powder supplied by two different supplier (further named as S1 and S2) was used as polymer material. N,N-Dimethylacetamide (DMAc, Lot. 121058 and 118329) supplied by Brenntag was used as a polymer solvent without further purification. As a pore forming agents salt of lithium (LiA, Lot. 110865) purchased from Brenntag and another low-molecular-weight organic compound (Lot. 118075 and 114386), further denoted as organic pore former (OPF), were used. Since LiA is a highly hygroscopic compound, it was dried in thermostatic chamber during 24 hours at temperature of 80°C before use. Water used for the coagulation bath was obtained by reverse osmosis. The alcohol applied for coagulation was used as received. Depending on the membrane type two different non-woven supports named H (average thickness 120 μm) and S (thickness 150 μm) were used.

3.2. Methods

3.2.1. Membrane preparation in laboratory scale

3.2.1.1. Casting solution preparation

PVDF solutions were prepared at different temperature regimes by mixing the polymer powder in the solvent (DMAc) in a glass beaker, followed by constant mechanical stirring until complete polymer dissolution (normally 2 hours). The range of the dissolving temperatures was dependent on the membrane type. In general the bottom limit was set as 20°C and the upper limit to 40°C. The dope composition was varied by adding different additives to the dope solution or/and by changing the polymer concentration. In case of LiA use, it was dissolved in DMAc before polymer addition. However, in case of OPF usage it was added after polymer addition because of its high volatility. After complete polymer dissolution the casting dope was kept at room temperature for at least 18 hours to remove air bubbles. In case if room temperature was higher than dissolving one, the solution was kept on water bath at the temperature not exceeding the dissolving one. The viscosity of prepared and degassed polymer solution was evaluated by viscometer (Brookfield, DV-E viscometer) at 25°C. If the dissolving temperature was lower than 25°C the measurements of viscosity were conducted after membrane preparation in order to prevent the alterations of the solution properties.

3.2.1.2. Casting method and apparatus

The flat-sheet membranes were prepared by phase inversion process induced by nonsolvent. The casting solution was manually cast onto a polyester non-woven fabric (Sanko or Hirose) with the aid of a casting knife. The casting thickness was carefully controlled and remains same as 540 or 580 μm depending on membrane type. The cast films were immersed in alcohol/DMAc or water/DMAc coagulation bath for at least 10 minutes. The composition of coagulation bath was precisely controlled by refractometer “Pocket refractometer PAL-1”, Atago, Japan. The effect of composition of water/DMAc coagulation bath on the membrane properties was done in the range of water content 15-70 wt.%. In case of alcohol/DMAc bath the limiting Brix% value was kept in previously determined range. After coagulation, membrane was transferred to the water washing bath to complete removal of the solvent and additives. The washed membranes were dried at 90°C in convection oven for at least 15 minutes. At same production conditions at least two similar membranes were prepared in order to insure the absence of mistake in obtained results.

3.2.2. Membrane preparation at industrial scale

The whole process of the casting solution preparation at industrial scale was conducted in 4 steps: components loading, mixing, filtration and degassing. The mixing procedure was performed during 6 hours instead of 2 hours in the laboratory. After preparation, the solution was transferred from the mixer to the storage tank. Between mixer and storage tank the filter was placed to remove large particles and non-dissolved agglomerates. Obtained solution was degassed at room temperature. Before membrane casting at industrial scale, the laboratory validation of prepared solution in terms of viscosity and membrane properties was done. During the industrial manufacturing the speed of support movement was set in agreement with standard membrane manufacturing protocol. The polymer solution was automatically cast onto a polyester non-woven fabric with the aid of the casting rolls with precise thickness control. The obtained film was immersed in the coagulation bath for at least 25 minutes. The nonsolvent mixture was continuously changed and circulated in order to keep the ratio solvent/nonsolvent and quantity of additives in coagulation bath in previously determined limits. For the determination of solvent and additives quantity in the coagulation bath the refractometer and conductometer "HI 8733" Hanna Instruments, USA, respectively, were used. Subsequently, the precipitated supported membrane was immersed in water washing bath to remove traces of solvent and additives for at least 30 minutes. The membrane was collected by rotating roll and subjected to continuous drying.

3.2.3. Membrane characterization

The membranes prepared in the laboratory were characterized in terms of air flow, critical water entry pressure and thickness. For the determination of air flow the circular sample with area of 3.7 cm^2 were cut and placed in the cell. This housing was assembled as shown on Fig. 11.

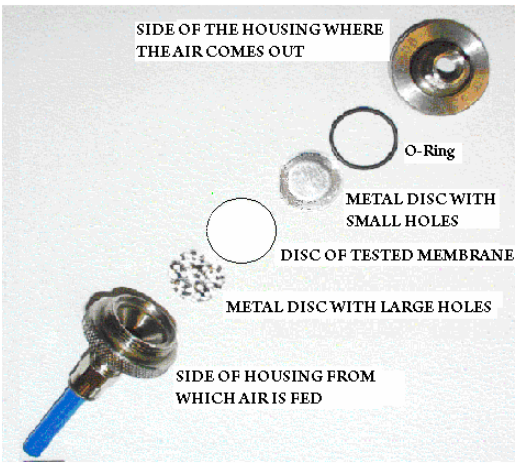


Fig. 11. Housing for the air flow measurements

The measurements of gas permeability through the membrane were performed under pressure of 0,930 bars (700 mmHg) for membranes Fortex 0.1 and Fortex 0.2 and 0,347 bars (260 mmHg) for membranes Fortex 1.2 and Fortex 3.0. The critical water entry pressure (water breakthrough (WBT)) was measured using the cell TA234 equipped with pump of maximum pressure equal to 5 bars. As soon as the sample was placed inside the device the pressure was continuously increased. WBT was considered as pressure at which the first water droplet appeared on another side of the membrane.

The membrane thickness was determined with micrometer Mitutoyo, Japan..

Apart from aforementioned analysis, membranes manufactured at industrial scale were also characterized by means of other techniques.

The morphology of prepared membranes was examined using Scanning Electron Microscopy (SEM). The samples were mounted on SEM stubs, and sputtered for 60 seconds for examination under an SEM (JEOL 6360). The images were taken under proper accelerating voltage and working distance. Some of the samples were fractured in liquid nitrogen to reveal the cross-sections for SEM observation.

The crystalline structure of fabricated membrane was analyzed by Fourier transform infrared spectroscopy. FT-IR spectra of fabricated membranes were recorded over the range of 4000–400 cm^{-1} with Bruker model Alpha ATR Diamond.

The membrane pore dimensions and their size distribution were determined by means of permporometry. The measurements were performed in a capillary flow porometer (CFP-1100-A-N). The circular disk samples were loaded into the sample holder, and a transmembrane pressure was gradually applied starting from either 5 psi (Fortex 0.1 and Fortex 0.2) or 0 psi (Fortex 1.2 and Fortex 3.0) until maximum pressure about 100 psi is reached, the resultant air flow is recorded and referred to as dry flow curve. Then the sample was saturated with a low surface tension fluid called Galwick (15.9 dynes/cm), and pressurized again, the recorded flow rate is referred to as wet flow curve. By inputting the parameters used in the measurements, like wetting fluid surface tension, etc., the porometry results were then automatically obtained through curve fitting of the dry flow curve and wet flow curve.

4. Results and discussion

The membrane formation by the phase inversion process induced by the nonsolvent means the transition of initially homogeneous solution into two equilibrium phases, because of solvent/nonsolvent exchange. One phase, usually referred as polymer-rich, results in the polymer matrix, while the second phase (polymer-lean) forms the pores inside. During the process of phase separation the polymer molecules can arrange in different structures which determine the morphology and properties of ultimate membrane. In principal, two different mechanisms of the membrane formation can be distinguished in case of PVDF material: liquid-liquid demixing and solid-liquid demixing (crystallization). Each of these mechanisms has a specific resulting structure and could be influenced by various parameters of membrane preparation process. The target of present research is to find the optimal production parameters which will allow fabrication of membranes with desired properties in terms of water repellency (or water breakthrough) and air permeability. In principal, the water breakthrough parameter of the membrane indicates the pressure at which the largest pore started to be wetted by water and this pressure is reciprocally proportional to the pore radius. The air permeability gives information about membrane porosity. In case of symmetric membrane, formed by solid-liquid demixing mechanism, this parameter indicates the porosity of the whole membrane, while in case of asymmetric membrane, resulted from liquid-liquid demixing process, only porosity of denser top layer is considered. In other words, if value of air flow is changed due to some alterations of membrane preparation conditions, this changes should be attributed to variation of total porosity of symmetric membrane or surface porosity of asymmetric one.

In order to achieve the target, the effect of different parameters on the ultimate membrane properties was studied. The techniques applied for the optimization of membrane production were: variation of polymer material (PVDF from different suppliers), changes of polymer dissolution temperature, modification of the casting solution composition by addition of additives of different nature and quantity, and alterations of coagulation bath composition. The starting point for each membrane type development as well as desired membrane properties were based on previous research conducted by R&D department of GVS Filter Technology Company and are presented in Table 3.

Table 3. The starting points and targeting parameters for all the membrane types

			Target properties	
Type of membrane	Initial composition DMAc:PVDF[a]:Pore former	Type of nonwoven [f] support	Air flow	Water breakthrough (WBT), bar
Fortex 0.1	99-X:X:1 (OPF) [b]	Type S	≥45 [d]	>6
Fortex 0.2	98-Y:Y:2 (OPF) [b]	Type S	≥430 [d]	≥1.8
Fortex 1.2	99-Z:Z:1 (LiA) [c]	Type H	≥40 [e]	≥0.35
Fortex 3.0	98-Z:Z:2 (LiA) [c]	Type H	≥100 [e]	≥0.15

[a] With respect to signed "Nondisclosure agreement" the exact composition of casting solution is hidden; however, relation between these values is X>Y>Z;
[b] Organic pore former (OPF) was suggested for Fortex 0.1 and Fortex 0.2 membranes;
[c] The salt of lithium was suggested for Fortex 1.2 and Fortex 3.0 membranes;
[d] measured in L/h/3.7 cm2 under the pressure of 0.930 bar (700 mmHg);
[e] measured in L/min/3.7 cm2 under the pressure of 0.347 bar (260 mmHg);
[f] the choice of nonwoven support was dictated by the peculiarities of further membrane processing into final filtration unit (membrane + housing);

4.1. Development of commercial membrane Fortex 3.0

The previously conducted research in the R&D department of GVS Filter Technology Company resulted in successful development of Fortex 3.0 with use of polymer S1. In order to protect company from such occurrence as unpredictable rise of price for certain material or problems with material supply the target to develop the protocol for Fortex 3.0 membrane production with use of polymer S2 was set. For this protocol development the salt of lithium was used as pore former. The standard mixture of alcohol and DMAc was used as nonsolvent. This type of coagulation bath usually referred as soft one [10] and, therefore, the predicted membrane formation mechanism is solid-liquid demixing (crystallization), normally resulted in particulate structure. This prediction will be further confirmed or disproved by means of scanning electron microscopy.

Since both polymers (S1 and S2) had almost the same characteristics basing on the information provided by suppliers it was decided that no drastic changes in casting solution compositions as well as in the composition of coagulation bath are required at the initial stage. Therefore, initially the influence of the polymer dissolving temperature on the ultimate membrane properties was studied. For this purpose the temperature range from 34°C to 40°C was applied. The obtained results are collected in Table 4.

Table 4. Properties (air flow, water breakthrough, thickness) of Fortex 3.0 membranes prepared at different dissolving temperatures

T_{dis}	*AF,L /min/3.7cm²*	*WBT, bar*	*Solution viscosity, cP*	*Thickness, µm*
34	50	0.22	1069	204
36	64	0.24	1063	201
37	75	0.16	1130	204
39	128	0.15	1010	205
40	178	0.13	1073	204
Target	≥ 100	≥ 0.15		>160

According to Table 4, the water breakthrough is steadily decreasing with the increase of polymer dissolving temperature. By applying 6°C warmer regime for casting solution preparation, the water repellency is reduced from 0.22 to 0.13 bars. This observation means that the formation of pores of larger sizes is favored at higher temperature. On the other hand, aforementioned increase of dissolving temperature was leading to the formation of membrane higher porosity, which is reflected by changes in air permeability from 50 to 178 L/min/3.7cm^2. Additionally, the most dramatic effect of solution preparation regime on the membrane air permeability was observed in the temperature range of 37 – 40°C, when this parameter was more than doubled, meaning that membrane porosity underwent significant increase.

The effect of dissolving temperature on the membrane structure was studied by Wang *et al* [63]. According to developed theory, at higher dissolving temperature the polymer coil has higher degree of expansion meaning that it is occupying more space inside the solution. In such situation the chains of polymer have more entanglements between each other. During the membrane formation by solid-liquid demixing each polymer coil represents the center of nucleation and due to larger size the process of growing is easier. Therefore, from the casting solution prepared at higher dissolving temperature the larger particles (crystallites) of PVDF are formed. Finally, taking into account that larger particles possess lower packing capability the larger pores between these particles are created. Consequently, the formed membrane will have more open structure, which ultimately results in higher

air flux through the membrane and its lower wetting resistance, the same effects as observed in present study.

Moreover, basing on this theory at higher dissolving temperature the solution viscosity should be slightly higher, due to presence of more entanglements between polymer chains. This effect was demonstrated by the authors of this theory. However, in the current study the range of applied temperatures is 10 times narrower, meaning that possibly this effect was not detected, due to the precision limitations of the used equipment. Nevertheless, the viscosity deviation of ±60 cP of prepared casting solutions was assumed to be not significant since it is only 5.6% of the actual value. From the membrane formation point of view, such insignificant variation of solution viscosity can not bring any changes to the solvent/nonsolvent exchange rate. In other words, in case of all the prepared casting solutions the diffusion of solvent from the cast film and nonsolvent inside the film during the phase inversion is the same, and, therefore, the kinetic effect of membrane formation is not affected [61].

Finally, the thickness of all fabricated membranes was almost the same. However, basing on previous conclusion about increase of membrane porosity, this parameter should be slightly higher at higher dissolving temperature applied. The difference between predicted and real results could be attributed to the fact that knife adjustment was done manually and without use of the digital devices. Thus, the real knife gap could have been not of the same width in all the cases. Another possible explanation is the nonuniform thickness of nonwoven support. According to the product characteristics provided by support supplier, its thickness can vary in the range 120±20 μm, meaning that the ultimate membrane thickness can also be variable.

Basing on the obtained results the dissolution temperature in the range of 38–39°C was selected for the industrial trial of Fortex 3.0 membrane fabrication with use of polymer S2, which is slightly different from optimal one for the polymer S1 (41°C).

4.2. Development of commercial membrane Fortex 1.2

For the development of Fortex 1.2 membrane salt of lithium as pore former and the standard mixture of alcohol and DMAc as nonsolvent were initially suggested as for the Fortex 3.0 project. However, for the current study the polymer and pore former content as well as PVDF type were different from the Fortex 3.0 membrane.

The first performed study in the frame of Fortex 1.2 membrane development was the determination of dissolving temperature influence on the ultimate membrane properties. The bench mark of this parameter was taken equal to 30°C. The results obtained in this part of research are presented in the Table 5.

Table 5. The influence of dissolving temperature on the performance of Fortex 1.2 membrane (1% of LiA)

T_{dis}	*AF, L/min/3.7cm²*	*WBT, bar*	*Solution viscosity, cP*	*Thickness, μm*
30	16.7	0.79	1159	167
32	27.0	0.56	1186	184
34	31.3	0.42	1153	190
Target	>40	0.35-0.4		>160

From the data in Table 5 results that the increase of dissolving temperature leads to the same changes of the air permeation and water repellency as in case of Fortex 3.0 membranes. The air flow was steadily increasing from 16.7 to 31.3 L/min/3.7cm^2, while the water breakthrough was continuously

decreasing from 0.79 to 0.42 bar over the increase of temperature of casting solution preparation from 30 to 34°C. Thus, the membrane porosity as well as maximal pore size is increasing at higher dissolving temperatures applied. This conclusion is in the agreement with membrane thickness measurements: thicker membranes were formed from casting solutions prepared in warmer conditions. Finally, similarly to the Fortex 3.0 project, the solution viscosity is not dependent on the dissolving temperature. Thus, all the observed tendencies could be attributed to the same factors as discussed in previous study.

Moreover, from Table 5, even at highest polymer dissolving temperature applied the membrane performance is not optimal and not meeting the requirements. The membrane fabricated from solution prepared at 34°C, exhibited the WBT of 0.42 bar, while the air flow was equal to 31.3 L/min/3.7cm^2. Evaluating the rate of membrane properties changes with respect to changes in their preparation conditions, it was concluded that simple alterations of polymer dissolving temperatures are not enough to achieve the target.

According to the literature review, the kinetic factor has higher influence on the membrane formation mechanism that the thermodynamic one [38]. Consequently, the next step was to alter the kinetics of solvent/nonsolvent exchange during the phase inversion process by addition of higher quantity of pore former to the dope solution. For this purpose the dissolving temperature of 30°C was utilized. The obtained results are collected in Table 6.

Table 6. The influence of lithium salt content in casting solution on Fortex 1.2 membrane properties

Content of LiA	*AF, L/min/3.7cm^2*	*WBT, bar*	*Solution viscosity, cP*	*Thickness, µm*
1	16.7	0.79	1159	167
1.5	18.7	0.73	1391	183
2	21.7	0.66	1630	174

Basing on the obtained results, membranes with more open structure are formed from the casting solutions with higher content of the lithium salt. This phenomenon can be attributed to the differences in the dope solutions viscosities. By increasing the LiA content from 1% to 2% the viscosity of solution increased from 1159 to 1630 cP. This effect is related to the formation of complexes between Li-ions and polar groups of DMAc and/or PVDF [58]. The increase of casting solution viscosity leads to the slowdown of the solvent/nonsolvent exchange, and, therefore, the liquid-liquid demixing is delayed giving more time for crystallization mechanism to occur. On the other hand, the salts of lithium are hydrophilic compounds, meaning that their presence can also enhance the influx of nonsolvent in the casting solution which is favoring to the former mechanism. Therefore, the ultimate membrane properties depend on the domination of one or another effect. According to obtained results, the influence of viscosity changes has greater effect on the membrane formation mechanism than the presence of the hydrophilic additive itself.

Moreover, from the Table 6 results, that the increase of the lithium salt in the casting solution has stronger effect on membrane porosity than on maximal pore size. Addition of 1% more of LiA to the dope solution leads to the air flow increase from 16.7 to 21.7 L/min/3.7cm^2 and to the decrease of critical water entry pressure from 0.79 to 0.66 bar. In other words, this variation of additive content enables the 30% increase of air permeation with only 15% sacrifice of WBT. Basing on these results and rate of membrane properties changes shown in Table 6, additional evaluation of dissolving temperature effect was required. For this study, the same conditions for membrane fabrication were applied, but this time preparing solution with the content of lithium salt equal to 2%. The results of this study are collected in Table 7.

Table 7. The influence of dissolving temperature on the performance of Fortex 1.2 membrane (2% of LiA)

T_{dis}	*AF, L/min/3.7cm²*	*WBT, bar*	*Solution viscosity, cP*	*Thickness, μm*
30	21.7	0.66	1638	175
33	42.8	0.37	1620	189
34	51.5	0.3	1625	183
Target	>40	0.35-0.4		>160

According to the obtained results the dissolving temperature at higher content of lithium salt has stronger influence on the membrane properties. Changing the temperature of casting solution preparation from 30°C to 34°C the increase of air flow was about 30 L/min/3.7cm^2, which is approximately 140%. In contrary, the same temperature variation in case of solutions containing 1% of inorganic additive resulted in only 87% gain of air permeability. The similar tendency was noticed with respect to the rate of water breakthrough changes. By increasing the dissolving temperature the WBT parameter was continuously decreasing. However, in case of 1% and 2% of LiA content in the casting solution the loss in water repellency was 0.37 bar (46%) and 0.36 bar (55%), respectively.

Finally, with the respect to the final target in terms of membrane properties, the desired values were obtained at the dissolving temperature of 33°C. Thus, for the industrial trial it was suggested to prepare the solution with LiA content of 2% and with use of the dissolving temperature equal to 33°C.

4.3. Development of commercial membrane Fortex 0.1

The previous research activity towards development of Fortex 0.1 membrane, conducted by R&D department of GVS Filter Technology Company, didn't give sufficient results and all the fabricated membranes possessed too low wetting resistance to be used for desired applications. Thus, the final decision concerning the optimal polymer type (S1 or S2) as well as appropriate membrane coagulation conditions was not done before current development process. However, the approximate composition of casting solution and type of pore former were determined (Table 3).

Basing on the literature review, the nonsolvents used for the PVDF precipitation could be categorized as: soft or weak (alcohols) and strong (water) and each of them favor to the different membrane formation mechanism. The difference between these types of nonsolvent is in the mass transfer of solvent from the casting film upon its immersion in coagulation bath. In case of using alcohol as nonsolvent, the mass transfer is slower, and, therefore, solid-liquid demixing is dominant mechanism, while the use of water coagulation bath enables fast mass transfer and as a result liquid-liquid demixing becomes dominant [38].

According to this fact, the comparison of properties of membrane prepared in the standard alcohol/DMAc bath with membranes, precipitated in harsh conditions with use of water/DMAc mixtures of different solvent content was essential for this project. Moreover, both S1 and S2 polymer were used to analyze this effect. For this purpose the solutions of two types of polymer with organic pore former (OPF) were prepared at the dissolving temperature of 20°C. The results of this part of the research are gathered in Tables 8 and 9.

The pure water was not used for membranes fabrication in this study. The reason for this is that industrial membrane manufacturing is the continuous process, and with every new piece of nonwoven support with the polymer solution on the top the new portion of DMAc is washed out to the coagulation bath, and, as a result its composition is changing. This side effect could be controlled by constant nonsolvent replacement, but in any case some part of DMAc will still be remaining. That is why, in order to avoid such complications it was decided to use only mixtures of water with solvent.

Table 8. Effect of coagulation bath composition on the performance of Fortex 0.1membrane prepared with use of polymer S1

Membrane	*Type of coagulation bath (wt%:wt%)*	*PVDF S1*				
		AF, L/h/3,7cm²	*WBT, bar*	*Water repellency at 6 bars*	*Solution viscosity,cP*	*Thickness, µm*
S1_A	DMAc/Alcohol	100	4,95	-	1643	185
S1_W30	DMAc:Water (70:30)	170	5	-	1643	186
S1_W50	DMAc:Water (50:50)	64	>5	+	1643	167
S1_W70	DMAc:Water (30:70)	20	>5	+	1643	173
S1_W85	DMAc:Water (15:85)	145	>5	-	1643	170
	Target	>45	>5	+	-	>160

Table 9. Effect of coagulation bath composition on the performance of Fortex 0.1 membrane prepared with use of polymer S2

Membrane	*Type of coagulation bath (wt%:wt%)*	*PVDF S2*				
		AF, L/h/3,7cm²	*WBT, bar*	*Water repellency at 6 bars*	*Solution viscosity, cP*	*Thickness, µm*
S2_A	DMAc/Alcohol	118	4,15	-	990	207
S2_W30	DMAc:Water (70:30)	500	2,4	-	990	195
S2_W50	DMAc:Water (50:50)	35	4,57	-	990	177
S2_W70	DMAc:Water (30:70)	15	4,7	-	990	171
	Target	>45	>5	+	-	>160

In comparison to the previous projects one additional target parameter "Water repellency at 6 bars" was set to be controlled. This requirement was related to the absence in laboratory of the pump which would be able to supply pressure higher than 5 bars, while the basic requirement concerning the membrane water repellency was at least 6 bars. Thus, the membranes with stability over 5 bars were additionally tested on industrial equipment allowing the measurements up to 6 bars.

From Tables 8 and 9 the first apparent difference observed was the significant discrepancy between the viscosities of casting solutions. In fact, the only difference between these solutions was the type of polymer used (S1 or S2), which leads to the conclusion that this inconsistency is a result of inherent properties of polymers. However, according to the material physicochemical indicators provided by the suppliers, both materials are almost identical. Thus, it was assumed that the possible reason was in the difference between polymer production conditions, for example, in the applied method of polymerization. From the membrane formation point of view, the difference in casting solution viscosity can result in the changes of the ultimate membrane performance, due to the aforementioned alterations of solvent/nonsolvent exchange kinetics. Practically, these changes became apparent when comparing results presented in Tables 8 and 9.

The effect of solvent addition to the water coagulation bath on PVDF membranes was demonstrated previously [6,8]. It was found that the precipitation power of the nonsolvent is decreasing with

increase of solvent addition. Thus, the phase inversion process is slowed down, and, therefore, the domination of formation mechanism in the membrane structure development is changing from liquid-liquid demixing to solid-liquid demixing. The former mechanisms results in finger-like structure with dense layer on the top, while the latter leads to the formation of symmetric sponge-like structure. Therefore, in the current study, by addition of different quantities of solvent to the coagulation bath, the influence of formation mechanism on membrane permeability characteristics was evaluated and compared to typical weak nonsolvent (mixture DMAc/alcohol).

From Tables 8 and 9, membranes prepared from both S1 and S2 PVDF in water coagulation bath with DMAc content up to 50% possess rather low air permeability and high WBT values. These results are related to the domination of the liquid-liquid demixing mechanism of membrane formation, and, therefore, to the formation of almost nonporous layer on the top. Additionally, all these membranes started to bend upon the immersion to the coagulation bath. This observation may be used as the visual primary justification of previous conclusion, because due to the presence of non-woven support the bottom part of membrane is stabilized, while the top part is able to shrink under influence of nonsolvent.

In particular, the S1_W70 and S1_W50 membranes allowed the air flow of 20 L/h/3,7cm^2 and 64 L/h/3,7cm^2, respectively. In parallel, both were remaining water repellent even under pressure of 6 bars. At the same time, membranes S2_W70 and S2_W50 exhibited the air permeation rates of 15 L/h/3,7cm^2 and 35 L/h/3,7cm^2, respectively, meaning that porosity of membranes prepared with use of polymer S2 is lower than that of S1. Moreover, their WBT indicators were 4.7 bars and 4.57 bars, respectively. Such a great difference in WBT values between membranes prepared in the same conditions, but from different polymers may be related to inherent differences between S1 and S2 materials. The only membrane deviated from the general trends was the one named S1_W85. In particular, this membrane was allowing the air permeability with the rate of 145 L/h/3,7cm^2, and its water repellency was lower than 6 bars. The reason for this is probably that used bath was too strong with respect to polymer precipitation, and therefore, the top layer underwent the microcracking due to excessive internal tension after shrinkage.

In contrary, according to the air flow and water breakthrough measurements the membranes S1_W30 and S2_W30 possessed more open structure. Moreover, in comparison to S1_W50 and S2_W50 higher solvent content in the coagulation bath had more dramatic effect on membranes prepared from the polymer S2. The great increase of air permeability from 35 to 500 L/h/3,7cm^2 was observed in this case. Such significant changes most probably are related to the shift of domination of one membrane formation mechanism over another. Basing on the obtained results it could be assumed that solid-liquid demixing occurred on the initial stage of structure formation. In addition, comparison of these results with the properties of membrane S2_A leads to the conclusion that the delay in liquid-liquid demixing was even longer and as a result larger crystallites had ability to be formed, and, consequently, larger pores were created between them. The similar changes in coagulation bath composition resulted in the same effect on the properties of membranes prepared from polymer S1. However, in this case observed changes were not such great. For membranes S1_W50 and S1_W30 the air flow parameter changed just from 64 to 170 L/h/3,7cm^2, while the decrease of WBT was a bit more than 1 bar. Finally, the performance of S1_W30 membrane was rather similar to S1_A, meaning that both used coagulation baths had approximately equivalent precipitation power with respect to the solution of polymer S1.

Evaluating the results with respect to the final target, only membranes S1_W50 and S1_W30 possess characteristics which are meeting or are close to the required ones. Thus, only these production conditions were selected for further membrane development process. However, since these membranes were prepared with use of another pore former in comparison to previous studies, the additional research about influence of such a crucial parameter as dissolving temperature was required. For this purpose all previously applied baths were analyzed with only one exception. Due to the fact that bath with DMAc content of 70% is not cost effective from a manufacturing point of view this type of nonsolvent was omitted. The results of these studies are presented in the Tables 10 –13.

Table 10. The influence of dissolving temperature on the performance of membranes prepared in standard alcohol/DMAc coagulation bath.

T_{dis}, ºC	AF, L/h/3,7cm^2	WBT, bar	Water repellency at 6 bars	Thickness, µm
20	115	4.9	-	183
22	195	4.18	-	185
24	326	3.16	-	192
Target	>45	>5	+	>160

Table 11. The influence of dissolving temperature on the performance of membranes prepared in coagulation bath DMAc:Water (15:85)

T_{dis}, ºC	AF, L/h/3,7cm^2	WBT, bar	Water repellency at 6 bars	Thickness, µm
20	145	>5	-	170
22	195	>5	-	179
24	240	4,8	-	182
Target	>45	>5	+	>160

Table 12. The influence of dissolving temperature on the performance of membranes prepared in coagulation bath DMAc:Water (30:70).

T_{dis}, ºC	AF, L/h/3,7cm^2	WBT, bar	Water repellency at 6 bars	Solution viscosity, cP	Thickness, µm
20	20	>5	+	1640	175
22	20	>5	+	1656	172
24	25	>5	+	1593	177
30	33	4.03	-	1632	161
Target	>45	>5	+	-	>160

Table 13. The influence of dissolving temperature on the performance of membranes prepared in coagulation bath DMAc:Water (50:50).

T_{dis}, ºC	AF, L/h/3,7cm^2	WBT, bar	Water repellency at 6 bars	Thickness, µm
20	64	>5	+	167
22	58	>5	-	168
24	41	4.94	-	175
Target	>45	>5	+	>160

From Tables 10 and 11, the same tendency in air flow and water breakthrough changes as in the previous projects was identified, meaning that in both soft and harsh conditions the dissolving temperature has the same effect on membrane properties. However, using the soft bath these changes were more dramatic. In case of alcohol/DMAc bath by applying 4°C warmer conditions for casting solution preparation the air permeability increased form 115 to 326 L/h/3,7cm^2, while the observed decrease in water repellency was from 4.9 to 3.16 bars. Similarly, utilizing the harsh bath the air flow increased from 145 to 240 L/h/3,7cm^2 and critical water entry pressure lost was steadily decreasing and at highest applied dissolving temperature was equal to 4.8 bars. Since none of formed membranes were meeting the requirement in terms of target properties, these production conditions were evaluated as unsuitable.

The unusual effect of dissolving temperature was observed in case of use of water coagulation bath with solvent content of 50% (Table 13). Oppositely to all other studies, with the increase of the casting solution preparation temperature the air flow as well as critical water entry pressure was decreasing. These results indicated that by applying higher dissolving temperature the membrane with lower porosity and larger maximum pore size is formed. The reason for such an unexpected deviation from normally observed trend is not yet understood, and it could be a subject for further research. Possibly it is related to the fact that membranes were cast from the solutions at the same temperature as they were prepared, meaning that these solutions had different viscosities. It is well known that reduction of temperature lead to the increase in viscosity, which from membrane formation point of view will result in slightly delayed liquid-liquid demixing allowing the formation of a bit more open structure. Evaluating results with the respect to the final target, the only membrane possessing sufficient properties was the one prepared with dissolving temperature of 20ºC. Therefore, these conditions were pre-selected for further industrial trial.

The effect of dissolving temperature on the membrane prepared with use of bath DMAc:Water (30:70) is shown in Table 12. It was demonstrated that the warmer conditions of polymer dissolution were leading to the formation of membrane with more open structure. In particular, the 10°C increase of dissolving temperature results in the slight raise of air permeability from 20 to 33 L/h/3,7cm^2. In parallel, the membranes lost their water repellency at 6 bars and the one prepared from solution mixed at 30°C was wetted at 4.03 bars. This result draw the conclusion that using this type of coagulation bath the target membrane can not be formed, at least without changes of the other parameters which are beyond the scope of current project. Thus, the only membrane meeting the target requirements was formed at 20°C and with use of coagulation bath DMAc:Water (50:50). Thus, these conditions were suggested for the further industrial trial.

The temperature of coagulation bath can affect the membrane formation process [65]. Since this type of nonsolvent was never used by GVS Filter Technology Company, the additional study about the influence of coagulation bath temperature on membrane properties was required. The range of analyzed temperatures was determined by its possible variations, which could be brought by changes of seasons. It was demonstrated (Table 14) that at analyzed range the coagulation bath temperature has no significant influence on membrane performance.

Table 14. Influence of coagulation bath DMA:Water (50:50) temperature on membrane properties

Bath T	*AF, L/h/3,7cm^2*	*WBT, bar*
19	67	>5
22	63	>5
25	64	>5
28	61	>5

As it stated previously the organic pore former (OPF) was used for the fabrication of all the membranes. However, this compound is highly volatile, meaning that during the industrial manufacturing process its content could be deceased in the dope solution. With respect to this possibility the additional study about the necessity of this compound usage was required. For this purpose the set of membranes was prepared without use of pore former (Table 15).

Table 15. Influence of dissolving temperature on membranes prepared without pore former and using DMAc:Water (50:50) coagulaton bath

T_{dis}, ºC	AF, L/h/3,7cm^2	WBT, bar	Stability at 6 bar	Solution viscosity, cP	Thickness, µm
20	44	>5	+	1564	163
23	34	>5	-	1590	164
26	21	5	-	1590	162
Target	>45	>5	+	-	>160

Comparing Table 13 and Table 15, it is evident that that the presence of pore former is mandatory for this membrane type. Due to its absence the air permeability decreased from 64 to 44 L/h/3,7cm^2, which is not acceptable in the frame of current project. Moreover, the viscosity of solutions prepared with and without OPF was slightly different: 1640 and 1590 cP, respectively. Thus, the presence of OPF has neglectable influence on casting solution viscosity, and, therefore, brings no changes to kinetics of membrane formation process. Owing to this similarity, the same tendencies in air flow and water breakthrough changes with variation of polymer dissolving temperature were observed. Consequently, it was decided not to make any changes in casting solution composition and suggest for the industrial trial conditions in which membrane S1_W50 was prepared.

Finally, the successful development of Fortex 0.1 membrane fabrication protocol with use of water is also attractive from the financial point of view. First of all, the alcohol substitution in the coagulation bath with water will lead to significant self-cost decrease since water is much cheaper. Secondly, the utilization of water as nonsolvent will give ability to decrease the use of organic solvents during production process, what is one of the principles of modern “Green Chemistry” concept. The latter will also bring financial savings, due to lower expanses for the production wastes disposal.

4.4. Development of commercial membrane Fortex 0.2

The previous research of the R&D department of GVS Filter Technology Company resulted in successful development of Fortex 0.2 with utilization of standard mixture alcohol/DMAc as nonsolvent. Currently, this type of membrane is a leader in the absolute quantity produced. Therefore, the purpose of current project was to decrease the cost of production process by substitution of alcohol with water coagulation bath.

The development of alternative protocol for membrane Fortex 0.2 manufacturing was directly dependent on the results of the research related to Fortex 0.1 membrane. At some point of previous project coagulation baths with compositions DMAc:Water (30:70) and (50:50) were evaluated as suitable for the obtainment of desired properties. Thus, at the initial point of Fortex 0.2 membrane development it was decided to fabricate membranes with use of both these bath compositions and compare the performance of prepared membranes with the industrially produced one. For this purpose the dissolving temperature of 24°C as well as polymer type S1 were applied. The same casting solution composition as in industrial production was used. The comparison of prepared membranes is presented in Table 16.

Table 16. Fortex 0.2 membranes prepared with use coagulation baths of different composition.

Type of coagulation bath (wt%:wt%)	*AF, L/h/3.7 cm^2*	*WBT, bar*	*Water repellency at 1 bar during 1 h*	*Solution viscosity, cP*	*Thickness, µm*
DMAc:Alcohol	440	2,3	+	1397	170-180
DMAc:Water (50:50)	64	>5	+	1397	179
DMAc:Water (30:70)	23	>5	+	1397	172
Target	>430	>1.8	+	-	>160

In comparison to the previous projects one new membrane characteristic "Water repellency at 1 bar during 1 hour" was set to be controlled. This requirement was dictated by the peculiarities of further membrane application, where specific water repellency is necessary under both dynamic and static conditions.

From the Table 16 results that use of water as nonsolvent leads to the formation of membranes with significantly tighter structure than in case of alcohol. Both membranes prepared in water coagulation bath with addition of 30% and 50% of solvent allowed the air permeability of 23 and 64 L/h/3.7cm^2, respectively, what is much lower than required. At the same time, both membranes possessed the resistance towards wetting higher than 5 bars instead of 1.8 bars required. According to the obtained results it was concluded that it is impossible to produce Fortex 0.2 with simple substitution of alcohol with water without other changes in casting solution composition.

As it was stated previously, the use of water as nonsolvent leads the domination of liquid-liquid demixing membrane formation mechanism, which results in the creation of dense structure. In contrary, the addition of solvent into coagulation bath and increase of casting solution viscosity can result in some delay of this mechanism, and, therefore more porous structure can be obtained. Basing on results of previous researches it was supposed that the substitution of OPF with salt of lithium without changes in ratio of components in casting solution can give desired result. For the verification of this prediction the coagulation bath with composition DMAc:Water (50:50) was selected, due to its relative weakness in comparison to DMAc:Water (30:70) bath with respect to membrane precipitation. Moreover, both polymer type (S1 and S2) were used in this study. Finally, as previously for the casting solution preparation the dissolving temperature of 24°C was utilized. Table 17 shows the difference between membranes prepared with use of OPF and LiA.

Table 17. Influence of type of pore former on membrane properties

Membrane	*AF, L/h/3.7cm^2*	*WBT, bar*	*Solution viscosity, cP*	*Thickness, µm*
S1 + OPF	64	>5	1397	179
S1 + LiA	209	3.75	2250	169
S2 + OPF	20	3.62	774	187
S2 + LiA	510	0.92	1328	193

As it was predicted the substitution of OPF with the same quantity of LiA resulted in dramatic increase of solution viscosity. In case of polymer S1 it changed from 1397 to 2250 cP, while using polymer S2 it raised from 774 to 1328 cP. Due to alteration of kinetics of solvent/nonsolvent exchange during polymer precipitation the properties of membrane were also modified. Owing to

aforementioned changes in casting solution composition the air permeability of membranes from S1 and S2 raised from 64 to 209 L/h/3.7 cm^2 and from 20 to 510 L/h/3.7cm^2, respectively. In parallel, the water repellency of both S1 and S2 membranes also underwent remarkable changes from >5 to 3.75 bars and from 3.62 to 0.92 bars, respectively.

With respect to the target of current research the only membrane S1+LiA possessed promising properties. It exhibited the twice lower air permeability and twice higher water repellency than required. As it was observed in previous projects the changes in polymer dissolving temperature can help to overcome this discrepancy. Thus, the effect of dissolving temperature on membranes prepared from polymer S1 and LiA as pore former was studied (Table 18).

Table 18. Effect of dissolving temperature on Fortex 0.2 membrane prepared from polymer S1 and LiA as pore former

T_{dis}, °C	*AF, L/h/3.7cm^2*	*WBT, bar*	*Water repellency at 1 bar during 1 h*	*Solution viscosity, cP*	*Thickness, μm*
24	209	3.75	+	2250	169
28	440	2.2	+	2228	168
30	510	1.3	-	2236	168
35	460	1.03	-	2293	173
40	470	0.85	-	2295	183
Target	>430	>1.8	+	-	>160

As it was predicted the variation of dissolving temperature gave ability to fabricate membrane with desired properties. The application of 4°C warmer conditions from the casting solution preparation results in the increase of air permeability from 209 to 440 L/h/3.7cm^2, while WBT decreased from 3.75 to 2.2 bars. At the same time membrane both membranes were remaining water repellent under pressure of 1 bar more during more than 1 hour. Thus, for the industrial trial it was suggested to use polymer S1 and LiA as pore former, dissolve them at temperature of 28°C and then coagulate in bath with composition DMAc:Water (50:50).

Finally, the analysis of dissolving temperature effect on membrane properties in large range of values revealed one important feature. After the temperature of 30°C, its further increase has almost no influence on membrane characteristics. In particular, the air flow was remaining around 480–510 L/h/3.7cm^2, while WBT value was kept as 1.1-1.3 bars over the whole range of applied temperatures. This last observation drove us to conclusion that the dissolving temperature is a crucial parameter only in specific range and after certain value has neglectably small effect on the properties of ultimate membrane.

4.5. Industrial manufacturing trials of developed membranes

The important stage in research and development activity of industrial company is a transfer of laboratory results to the industrial scale production. In order to verify if suggested production parameters are suitable for large scale production the set of additional trials was performed.

The first industrial scale trial was performed with membrane Fortex 3.0. The target was to evaluate possibility of this membrane type production with use of both polymers S1 and S2, since just before current study the protocol for polymer S1 was developed and wasn't verified at industrial scale. Results of the first trial are collected in Table 19.

Table 19. First industrial trial of Fortex 3.0 membrane with use of polymer S1.

	T dis,°C	*AF, L/min/3.7cm²*	*WBT, bar*	*Thickness, µm*
Indust. Results, beginning	42	126	0.14	159
Indust. results, after 90 min	42	74	0.18	153
Indust. results, after 180 min	42	54	0.20	151

From the Table 19 results that with the course of production some properties of the process changed and this lead to the formation of membranes with tighter structure (lower porosity and lower maximal pore size). After 3 hours of continuous production the air permeability of manufactured membrane decreased from 126 to 54 L/min/3.7cm^2, while water repellency increased from 0.14 to 0.20 bars. In fact, at the beginning of the process the properties of the membrane were very close to the desired ones; however, the reason for such remarkable deviation was to be identified. In order to prove that the source of the problem was not in the step of solution preparation, the next trial in the same conditions was performed (Table 20).

Table 20. Second industrial trial of Fortex 3.0 membrane with use of polymer S1

	T dis,°C	*AF,L /min/3.7cm²*	*WBT, bar*	*Thickness, µm*
Indust. results, beginning	42	125	0.13	157
Indust. results, after 90 min	-//-	72	0.17	160
Indust. Results, after 180 min	-//-	51	0.19	159

Basing on the results of this trial, it was demonstrated that the source of problem was not in the casting solution preparation stage. The obtained results of first and second trials showed almost identical results: at the beginning of production the air flow through the membrane was 126 and 125 L/min/3.7cm^2, respectively. Similarly, the critical water entry pressure was equal to 0.14 and 0.13 bars, respectively. After 3 hours of production the air permeability dropped more than twice to the value of 51 L /min/3.7cm^2, while the WBT parameter gain additional 0.06bars. With respect to the obtained result the next hypothesis was developed. It was predicted that the performance of produced membranes are changing due to changes in water content of the casting solution. Verification of this hypothesis was performed in the laboratory scale (Table 21).

Table 21. Influence of water content in casting solution on membrane properties

Time, days	*Water content, %*	*AF, L/min/3.7cm²*	*WBT, bar*	*Thickness, µm*
0	0.5	89	0.15	199
0.5	1.2	92	0.16	193
1	2	85	0.17	220
1.5	2.7	82	0.18	215
2	3.04	76	0.19	220
3	4.23	Start of gelation		

From the Table 21, the higher water content leads to the formation of membrane with lower air permeability and higher water repellency. In particular, moving from 0.5% to 3.04% of water in the casting solution the former parameter was gradually decreasing from 89 to 76 L/h/3.7cm^2, while latter was steadily increasing from 0.15 to 0.19 bars. Finally, at the water content of 4.23% the gelation

process started to occur. The observed effect was attributed to the changes in thermodynamic aspect of membrane formation. Water is nonsolvent for PVDF and its presence in casting solution brings the system closer to binodal. Thus, after membrane immersion into coagulation bath the time before start of liquid-liquid demixing is reduced, and, therefore, solid-liquid demixing has shorter period to occur. Thus, membrane with relatively tighter structure is formed from the solution with higher water content. Basing on this conclusion, maximal protection of the production system from the environmental humidity during the manufacturing process is required.

In parallel to the verification of previous hypothesis, the industrial trial of Fortex 3.0 membrane with use of polymer S2 was conducted. Basing on Tables 19, 20, it was found that during industrial manufacturing the membrane with higher air flow indicators is produced, in comparison to the laboratory test. Therefore, for the industrial trial of the initially suggested temperature of 38–39°C was changed to 36.5-37.5°C. During this study the humidity protection was applied. The obtained results are presented in Table 22.

Table 22. Industrial trial of Fortex 3.0 membrane with use of polymer S2

	T dis,°C	*AF, L/min/3.7cm^2*	*WBT, bar*	*Thickness, µm*
Laboratory results	39	128	0.15	200
Indust. results, beginning	37	110	0.15	168
Indust. results, after 90 min	-//-	114	0.15	164
Indust. results, after 180 min	-//-	114	0.14	162
Indust. results, after 270 min	-//-	118	0.13	166
Target	-	≥100	≥0.15	150-200

From Table 22 results that the results obtained during laboratory membrane development are reproducible at industrial scale. However, for the large scale production the applied dissolving temperature was 2°C lower than the one found to be optimal during laboratory testing. This slight mismatch is attributed to the differences between “batch” laboratory membrane preparation process and “continuous” industrial manufacturing. The fabricated membranes were taken for assembling into final filtering device in order to prove feasibility of its usage for particular application.

The next membrane type tested at industrial scale was Fortex 1.2. The casting solution was prepared at the temperature of 34°C, and, therefore, predicted membrane properties were a bit worse than required. Thus, the target of this trial was to evaluate the possibility to reproduce the laboratory results at industrial scale (Table 23).

Table 23. Industrial trial of Fortex 1.2 membrane

	T dis, °C	*AF, L/min/3.7cm^2*	*WBT, bar*	*Thickness, µm*
Laboratory results	34	51.5	0.30	183
Industrial, beginning	34	49	0.30	157
Industrial, after 60 min	34	47	0.32	150

According to the obtained results the properties of membrane prepared in laboratory were perfectly reproduced at industrial scale at long term manufacturing process. Moreover, the significant changes in ultimate membrane thickness brought no evident alternations to the air flow and water repellency indicators.

The third membrane type manufactured industrially was Fortex 0.1. Basing on laboratory research the suggested dissolving temperature was 20°C. This basic requirement was fulfilled; however, during the degassing step the solution was warmed up to the room temperature. Additionally, the coagulation bath was also warmer than desired. Both these changes are leading to the changes of kinetic factor of membrane formation. In first case, due to higher solution temperature its viscosity got lower, which together with warmer coagulation bath is leading to facilitation of solvent/nonsolvent exchange during coagulation. This results in stronger domination of liquid-liquid demixing over solid-liquid one, and, therefore, the formation of membrane with denser structure was predicted. The results of this trial are collected in Table 24.

Table 24. Industrial trial of Fortex 0.1 membrane

	T dis, °C	*AF, L/h/3.7cm²*	*WBT, bar*	*Water repellency at 6 bars*	*Thickness, µm*
Laboratory results	20	64	>5	+	167
Industrial, beginning	20*	35	>5	+	156
Industrial, after 60 min	20*	40	>5	+	159

* during the degassing the solution was warmed up to room temperature

According to the obtained results, our theoretical prediction was correct and membranes with significantly denser structure were manufactured.

The last industrial trial was performed for membrane Fortex 0.2. All the manufactured membranes showed unexpected defects that could not be solved quickly, for example adjusting the casting parameters. Due to this, it was impossible to find the region for the analysis. Probably, the reason for such a problem is in the high solution viscosity of the casting solution. Therefore, the manufacturing line improvements or/and further research about possibility to transfer the production of Fortex 0.2 from laboratory to the industrial scale, using water bath, are required. In the same time, the manually prepared membrane from the same solution exhibited identical properties to the previously found during the laboratory development, meaning that the failure of industrial trial was related to the settings of production line.

Finally, in order to summarize the results, the developed membranes were compared with the properties of ones which are currently purchased from other companies and placed in the housings manufactured by GVS Filter Technology (Table 25).

Table 25. Fortex membranes comparison with competitors [72,73].

GVS Filter Technology			*Competitor A.*		*Competitor B*	
	Air Flow	WBT, bar	Air flow	WBT, bar	Air flow	WBT, bar
Fortex 0.1	35-40	>6	-	-	45	>5
Fortex 0.2	430*	2.2*	>280	>1.79	>90	>3
Fortex 1.2	47	0.32	37.8	0.41	-	-
Fortex 3.0	110	0.15	>60	0.21	-	-

* laboratory results

According to Table 25, the developed membranes possess similar or even exceeding properties to the currently used ones, purchased from Competitor A or /and B, meaning that it is reasonable to assemble them into the filtering devices. In case, their performance is sufficient, internal membrane production can be started, and, obviously, it will bring significant decrease of the final product self cost.

4.6. Characterization of industrially manufactured membranes

4.6.1. Morphology of prepared membranes

Scanning electron microscopy images with different magnification of manufactured membranes are presented in Fig. 12–15. The effect of nonsolvent strength on the membrane structure is evident here: membranes Fortex 0.1 (Fig. 12), Fortex 0.2 (Fig. 13) coagulated in mixture DMAc:Water (harsh bath), and, Fortex 1.2 (Fig. 14), Fortex 3.0 (Fig. 15) fabricated with use of standard mixture DMAc:Alcohol (soft bath).

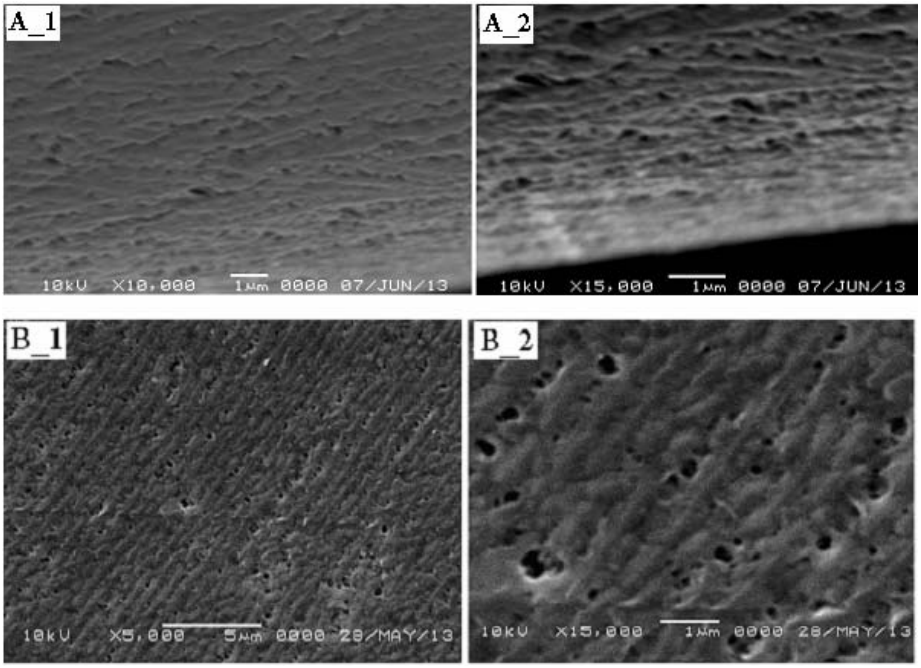


Fig. 12. SEM microphotographs showing the cross section (A_1 and A_2) and top layer (B_1 and B_2) of Fortex 0.1 membrane

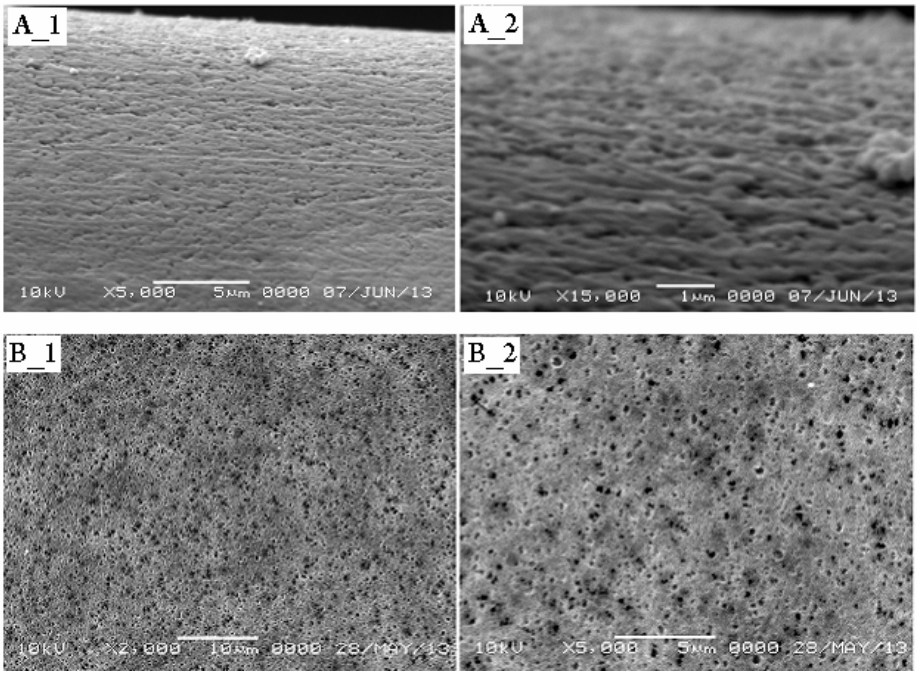


Fig. 13. SEM microphotographs showing the cross section (A_1 and A_2) and top layer (B_1 and B_2) of Fortex 0.2 membrane

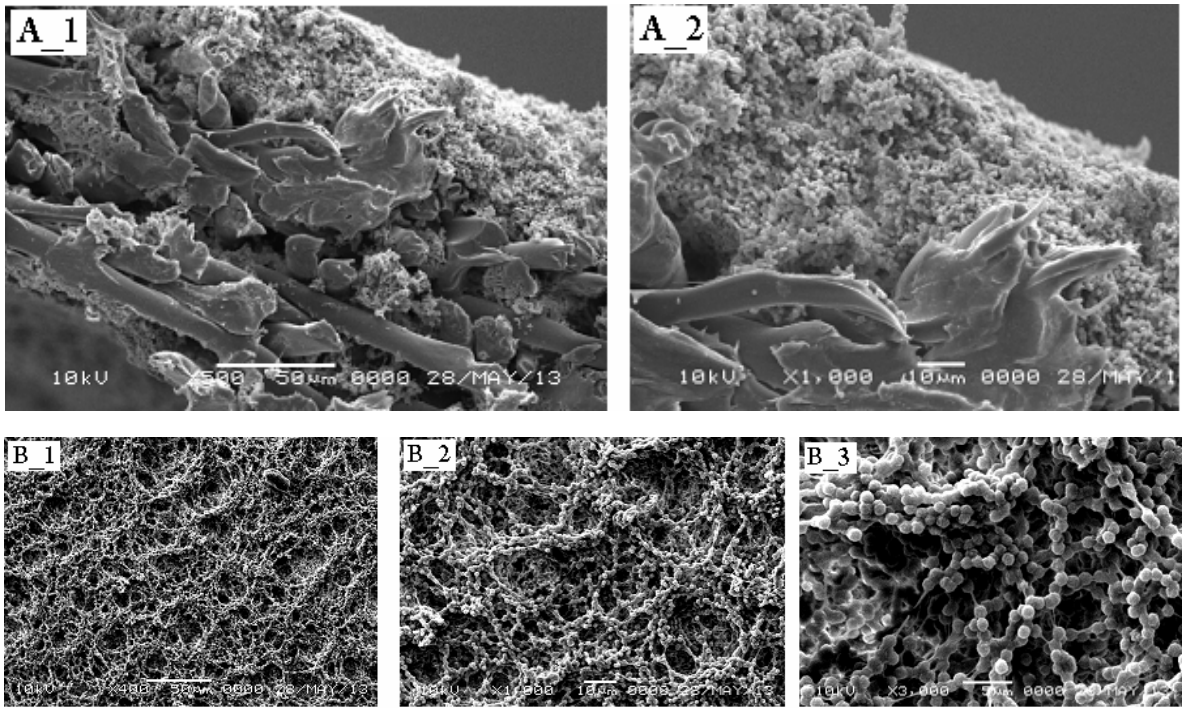


Fig. 14. SEM microphotographs showing the cross section (A_1 and A_2) and top layer (B_1, B_2 and B_3) of Fortex 1.2 membrane

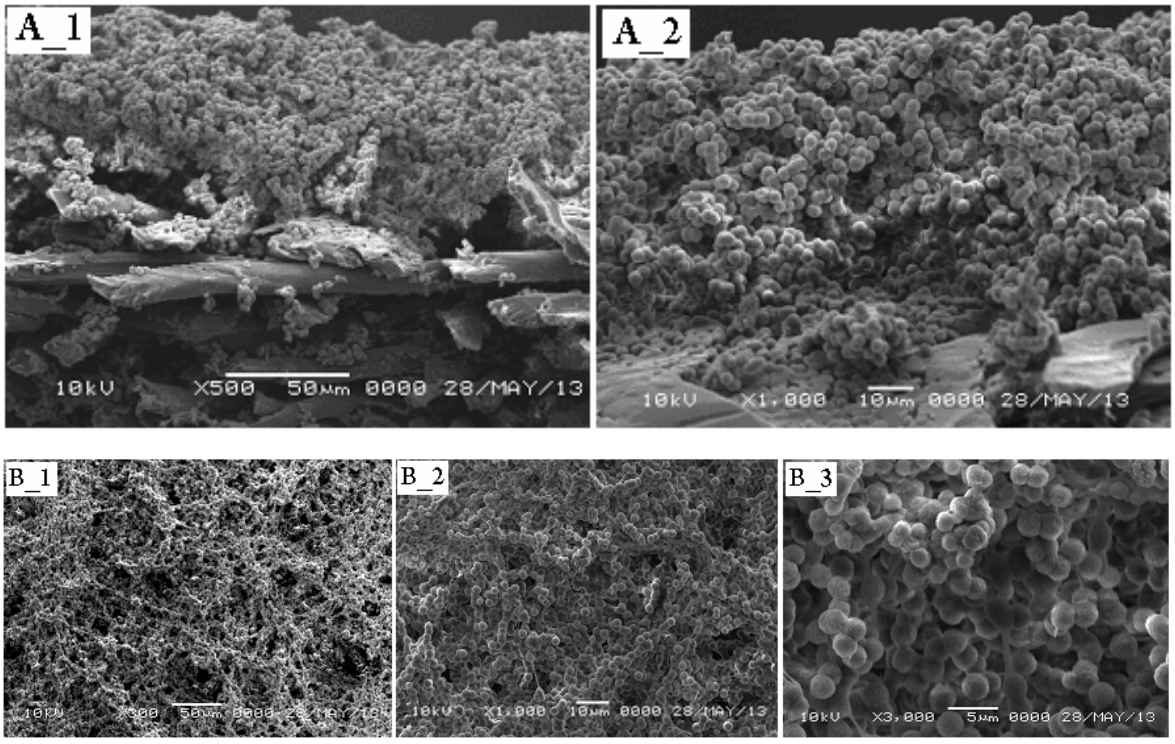


Fig. 15. SEM microphotographs showing the cross section (A_1 and A_2) and top layer (B_1, B_2 and B_3) of Fortex 3.0 membrane

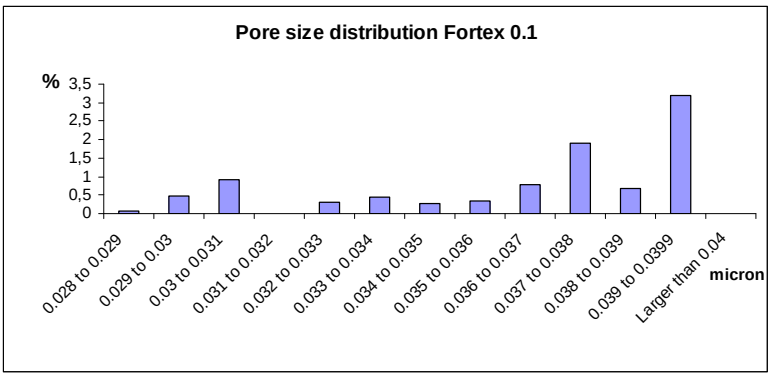
The PVDF membranes precipitated from the harsh bath, as shown in Fig 12 and 13, exhibit relatively dense structure form cross-section angle, while distinct pores are observed from the top side. Moreover, the dimension and total number of pores in the top layer are expectably larger for Fortex 0.2 membrane that for Fortex 0.1, which is in the agreement with the measurements of air

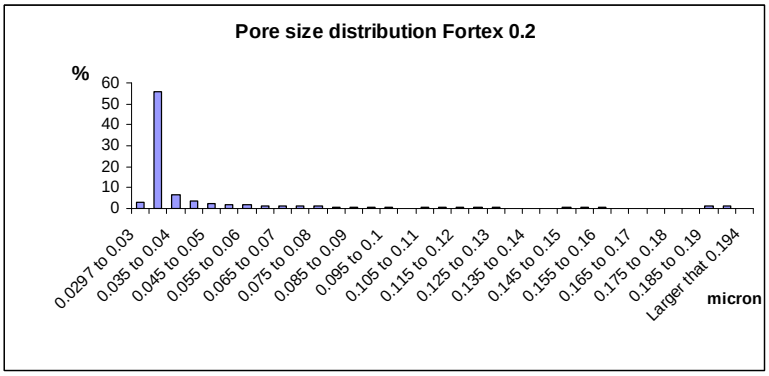
permeability and water repellency. Since typical structure resulted from crystallization (interconnected crystallites) is not observed, the resulted structure formation was governed mainly by liquid-liquid demixing. However, from typical ternary phase diagram, due to solvent/nonsolvent exchange the system initially is brought to metastable region, where solid-liquid demixing should occur, and only after this, system enters the zone, where liquid-liquid demixing takes place. Basing on this consideration the obtained structure should possess crystalline particles. Nevertheless, the process of nucleation and growth requires significant time and, therefore, the crystallites are created only if the liquid-liquid demixing is strongly suppressed. Fig. 12 and 13 prove that liquid-liquid demixing was dominating membrane formation mechanism, meaning that the metastable region was passed rapidly and crystallization had not enough time to occur. The observed morphology of these membranes is not completely conforming to the ones observed by other researchers. Normally, by using the harsh coagulation conditions the membranes with dense top layer with "finger-like" structure beneath are obtained. The fact the our membranes exhibited not the same morphology can be attributed to the presence of nonwoven support, which alter the solvent/nonsolvent exchange rate upon membrane immersion into coagulation bath.

In contrary, the morphology of membranes Fortex 1.2 and Fortex 3.0 precipitated in alcohol bath differed from Fortex 0.1 and Fortex 0.2. Fig.14 and 15 show a uniform structure composed of spherical particles. These crystallites are approximately of the same size of 1 μm and 1.5-3 μm, respectively, meaning that all crystallites nucleated and grown in similar concentration conditions. The obtained structures resulted from typical crystallization-dominated coagulation. In these cases, the liquid-liquid mechanism was sufficiently suppressed by slow solvent/nonsolvent mass exchange, and, therefore, solid-liquid demixing had sufficient time to occur.

4.6.2. Liquid expulsion permporometry

One of the most important characteristics of membrane is the pore size distribution. Even though for membranes developed in current work the main parameter is the size of largest active pore, the knowledge about total pore size distribution is of high importance. The identification of active pores in manufactured membranes as well as dimension of their mean flow pores was done by means of the liquid expulsion permporometry (Fig. 16).





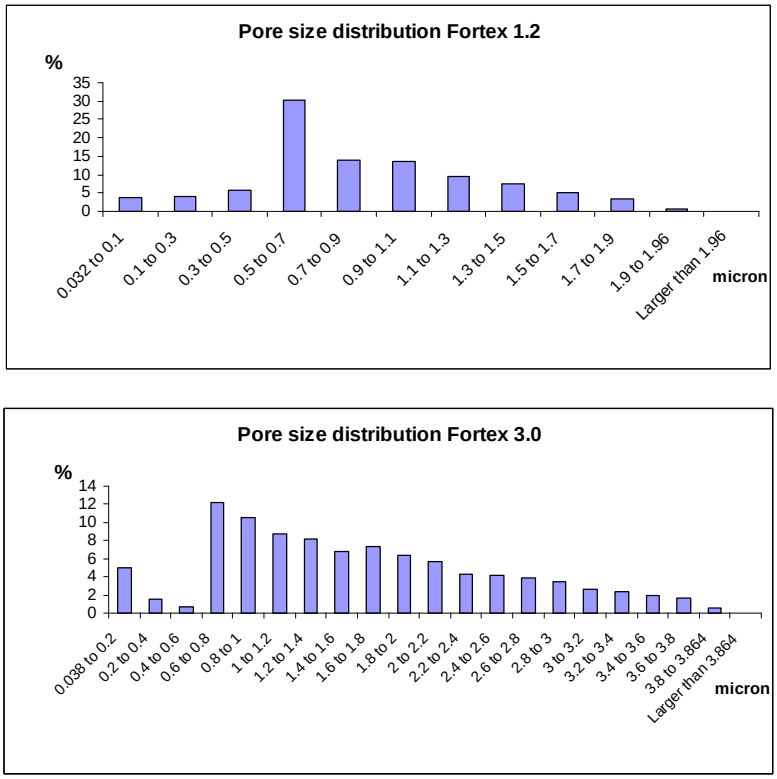


Fig. 16. Pore size distribution of manufactured membranes

As it shown in Fig. 16, the membrane Fortex 0.1 possesses the largest and most abundant pores with radius of 0.04 μm. Thus, these pores make the most significant contribution to gas transport and have highest propensity to be wetted by water. Since the limiting pressure for the used equipment is 100 psi (6.9 bars) the smallest detected pore is of size 0.028 μm. The total percentage of found pores is around 9.5%, meaning that all other pores are smaller and are not detectable by used equipment. The maximal pore size detected in membrane Fortex 0.2 is equal to 0.194 μm and the most abundant one has radius in the range 0.035 – 0.04 μm. For this membrane type almost 90% of pores were detected. Thus, the undetected pores are of less importance in terms of mass transport.

Concerning membranes fabricated in soft conditions the results reflecting the presence of more open structure were obtained. The maximal pore sizes of Fortex 1.2 and Fortex 3.0 membranes were 1.96 μm and 3.864 μm, respectively. The most numerous pores (30%) in former membrane were detected in the range of 0.5–0.7 μm. While in latter membrane the pore size distribution was considerably wider. The quantity of pores with particular size was steadily increasing from largest ones and reaching maximum of 12.2% in the range 0.6–0.8 μm. Finally, since both Fortex 1.2 and Fortex 3.0 membranes possess rather open structure virtually all pores were detected: 97.5% and 98%, respectively.

4.6.3. Crystalline structure of manufactured membranes

The preparation conditions apart from transport characteristics also influence the crystalline structure of PVDF membrane. The types of crystalline phases present in fabricated membranes were determined by means of Fourier Transform Infrared Spectroscopy. The obtained spectra are presented on Fig. 17-20.

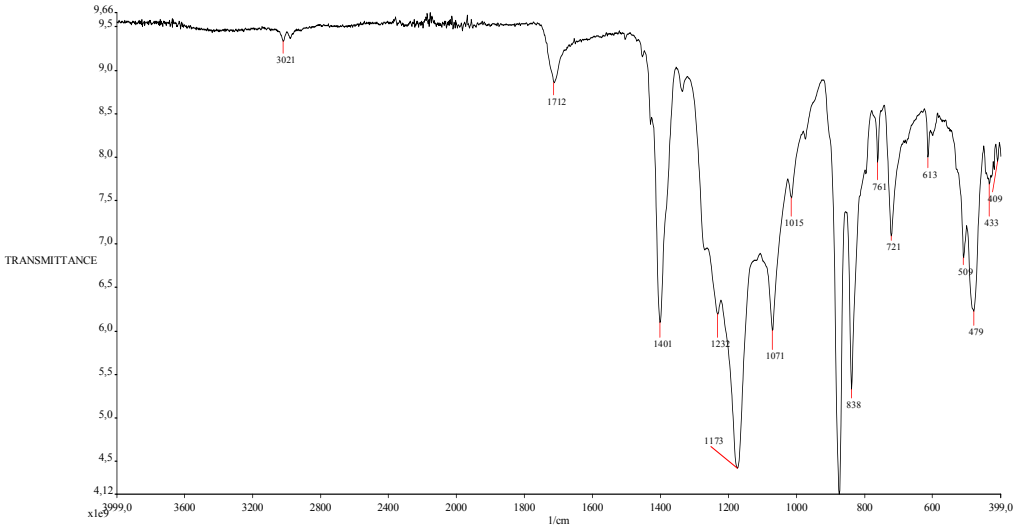


Fig. 17. FT-IR spectrum of Fortex 0.1 membrane

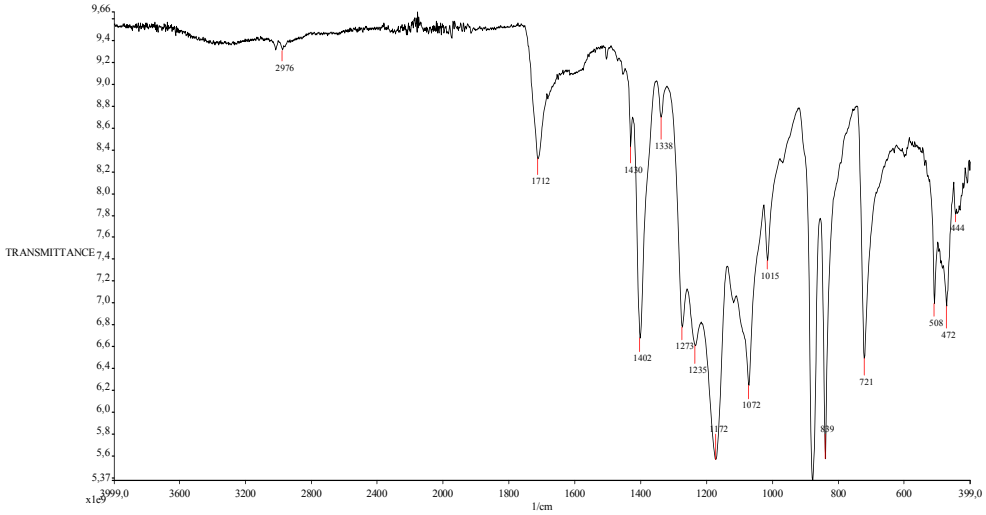


Fig. 18. FT-IR spectrum of Fortex 0.2 membrane

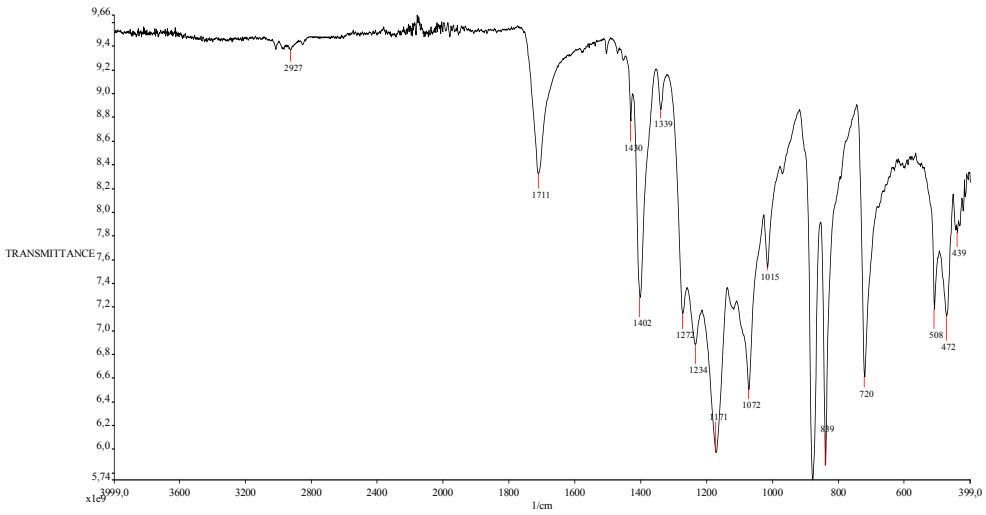


Fig. 19. FT-IR spectrum of Fortex 1.2 membrane

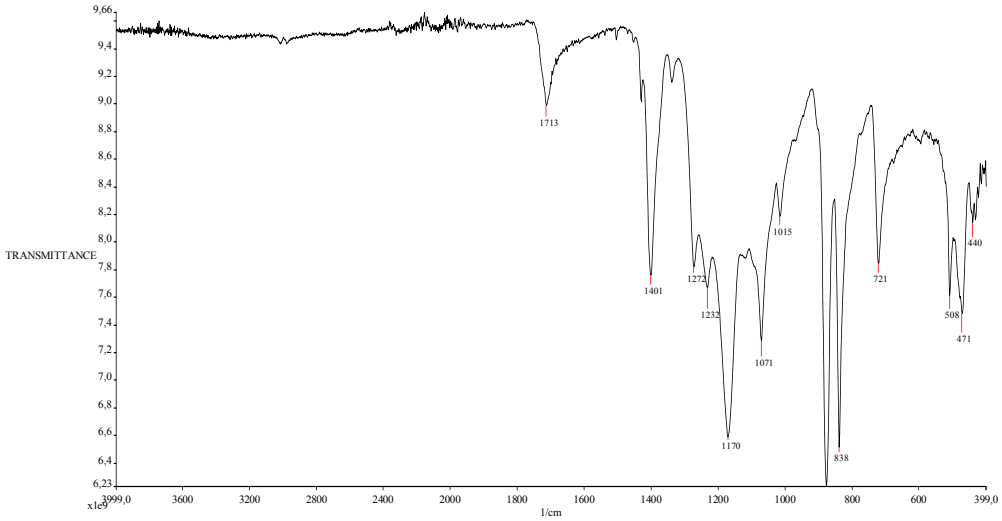


Fig. 20. FT-IR spectrum of Fortex 3.0 membrane

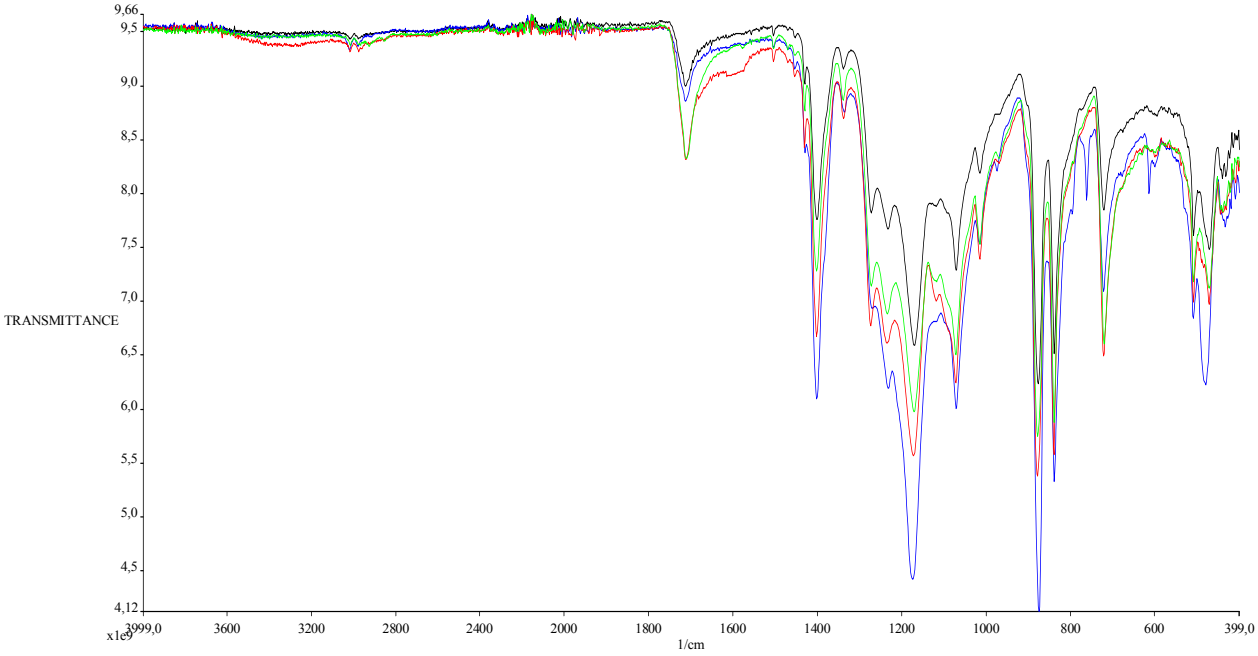


Fig. 21. Combined spectrum of all four manufactured membrane types
(Fortex 0.1 – blue, Fortex 0.2 – red, Fortex 1.2 – green, Fortex 3.0 - black)

Although the large effort directed to interpretation of infrared (IR) spectrums of PVDF was done, some contradictions are still present [74]. Therefore, in order to prove one or another crystalline structure presence an additional testing is required, for example X-ray diffraction analysis or/and differential scanning calorimetry measurements. Thus, the description of obtained results may possess certain level of inaccuracy.

In Fig. 17, basing on different literature sources [38,74] two or three crystalline structures could be defined. The absorbance bands at 509, 479 and 838 cm^{-1} could be attributed to the β-phase; however, last two peaks may be also reflecting the presence of γ structure. Additionally, the α phase characteristic peaks at 613 and 761 cm^{-1} of very low intensity are observed, meaning that the formation of this polymer chain arrangement is not favored in applied membrane preparation conditions. Apart from this, the peaks at 1232 and 1272 cm^{-1}, which are attributed to C–F bong out-of-plane deformation in γ and β phase, respectively, provide addition justification of presence of all three crystalline forms in analyzed membrane.

According to the Fig. 18-20 the membranes Fortex 0.2, Fortex 1.2 and Fortex 3.0 possess the crystals only of γ and β-structure. The latter can be detected in all the samples by the presence of characteristic peaks at 472(471), 1272(1273), 839(838) and 508 cm^{-1}, while the former is found by bands at 1234 and 1235 cm^{-1}, depending on the sample. Basing on this observation, such changes in membrane manufacturing conditions as polymer dissolving temperature and type of coagulation bath have no significant impact on the qualitative crystalline structures formation.

Finally, in order to compare the obtained spectra from quantitative point of view, all of them were laid one over another on Fig. 21. The intensity of peaks at 479, 840 and 1234 cm^{-1} is changing in the following sequence Fortex 0.1>Fortex 0.2>Fortex 1.2>Fortex 3.0. In case of band at 508 cm^{-1} the same order is remaining with only one exception: its intensity for Fortex 0.2 and Fortex 1.2 membranes is almost identical. These results lead to the conclusion that the membrane type Fortex 0.1 possesses the highest degree of crystallinity. This finding is different from the predicted one. According to the SEM analysis the Fortex 1.2 and Fortex 3.0 membranes are composed of crystalline particles, while on images of other two membranes no crystallites were observed. Thus, the former two membranes were believed to have higher degree of crystallinity. Such a deviation between theoretical and practical results could be attributed to two reasons. Firstly, the membranes with smaller pore sizes may contain some traces of DMAc entrapped inside very small pores, and its presence can affect the intensity of peaks in "finger print" region of the spectrum. Secondly, this effect could be explained by the differences in nonwoven supports used. Since they are supplied by two manufacturers, the polyether could have slightly different chemical structures and, therefore, infrared spectrums.

4.7. Applications of developed membranes

After the successful membrane development and laboratory testing each membrane is assembled to the final device for particular application. The list of developed membranes and their applications are presented in the Table 26.

Table 26. Applications of developed membranes

Membrane type	Application
Fortex 0.1	Venting in infusion filters for drug delivery and parenteral nutrition
Fortex 0.2	Transducer protector
Fortex 1.2	Bacterial Air Vent
Fortex 3.0	Bacterial Air Vent

Fig. 22. Applications of developed membranes.
"IV Express" filter (left), Bacterial Air Vent (middle) and transducer protector (right).

Intravenous (IV) infusion filter are designed to prevent the human blood-vascular system from the particles, which could be formed in the injected solution. There are different sources of these particles: spallation of silicone or polyvinyl chloride fragments from tubing [75], agglomerations of poorly soluble drugs [75] etc. The entry of these particles to the blood stream can cause side effect of treatment called phlebitis. Moreover, the infusion filters remove air from the fluid, and, there for protect patient from venous air embolism [76]. That is why infusion filters have an integrated hydrophobic membrane which enables them to remove present gas bubbles from infusion solutions.

Transducer protectors is a membrane filter which is used in hemodialysis device to keep the blood side of the circuit separated from the machine side. It prevents the contamination of the machine by the blood flowing through the circuit. This contamination could be dangerous and can lead to patient cross infection with hepatitis B or other virus. Transducer protectors allow air to pass while preventing the blood from passing through. The key element of this device is a hydrophobic bacterial retentive membrane with the pore size of around 0.2 μm [77].

Many medical devices require vents to keep their internal pressure balanced with the ambient pressure. This avoids deformation of rigid plastic containers and interruptions in flow of fluids. Developed Bacterial Air Vent must protect the fluid path from bacterial contamination (must maintain sterility). One good example of this is maintaining sterility of an IV set, and the equalization of the internal pressure of the bottle with solution via a vent on the spike. Venting characteristics are obtained by using hydrophobic membranes. According to the fact that filtering bacteria in air is about 10 times more efficient than in water, the use of hydrophobic membranes of 1.2 or 3 micron is sufficient to filter bacteria Brevundimonas diminuta to the same extent as 0.2 μm hydrophilic membrane during liquid filtration [78].

Conclusion and further perspectives

Four membranes with commercial names Fortex 0.1, Fortex 0.2, Fortex 1.2 and Fortex 3.0 were developed at the laboratory scale. The influence of the production conditions, such as polymer dissolving temperature, strength of coagulation bath, presence and type of additives and coagulation time, on the ultimate membrane properties was defined. It was demonstrated that the increase of temperature of casting solution preparation is leading to the formation of membrane with more open structure. The only exception from this trend was observed for Fortex 0.1 membrane; however, the hypothesis for its explanation was provided. Moreover, it was observed that the addition of solvent to the coagulation bath gives ability to decrease its precipitation power with respect to polymer, and, therefore, change the domination of one membrane formation mechanism over another.

The membrane preparation protocols developed at the laboratory scale were implemented for the industrial production. It was demonstrated that the good reproducibility of results after scale-up of production can be achieved. Slight deviations between laboratory and industrial prepared membranes were discussed.

All the industrially manufactured membranes were subjected to additional characterization. The SEM analysis revealed that membranes prepared in harsh conditions possess almost dense structure, while the onces precipitated in soft nonsolvent exhibited the particulate structure, which is the typical for solid-liquid demixing membrane formation mechanism. Moreover, the differencies in air permeability and water repellency between developed membranes were demonstrated by results of liquid expulsion permporometry (maximal pore size). Finally, the presence of certain crystalline structures was determined by FT-IR. It was demonstrated that all the membranes have β and most probably γ phases, and, apart from these, the membrane Fortex 0.1 exhibited the presence of α structure. These results revealed that the differences in preparation conditions between manufactured membranes has no significant influence on type of crystalline structures formed.

Basing on the research findings from this work, the following are recommended for further studies in future.

1) The optimal polymer dissolving temperature for Fortex 0.1 membrane was defined as 20°C. However, due to changes of seasons the temperature in production zone can vary dramatically and in summer time can excess this value. In this situation, during the solution degassing the solution will be warmed up that can result in undesired alterations of the membrane properties. Therefore, the additional study with the aim to find the way how to increase the optimal dissolving temperature is required.

2) The increase of polymer dissolving temperature in case of Fortex 0.1 was leading to the decrease of air permeability. Although the preliminary hypothesis was offered, the more complete research of this effect is of high importance and should be performed in further studies.

3) The observed morphology of membranes fabricated in harsh conditions was not conforming with results of other researches. The hypothesis explaining this discrepancy was related to the presence of nonwoven support. However, the practical justification of this idea has to be performed in future.

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